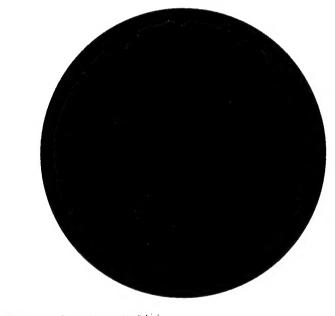
#### PROGRAM and ABSTRACT BOOK

# 16th International Liquid Crystal Conference



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Charachanian Unlimited

June 24-28, 1996

Kent State University Kent, Ohio, USA

19971204 159



By Philip L.Taylor, Case Western Reserve University

#### PROGRAM and ABSTRACT BOOK

# 16th International Liquid Crystal Conference



June 24-28, 1996

Kent State University Kent, Ohio, USA

## 16th International Liquid Crystal Conference

Organized by
Department of Physics
Department of Chemistry
and
Liquid Crystal Institute

#### **Kent State University**

Under the Auspices of

International Liquid Crystal Society

Sponsored by ALCOM\* Samsung Electronics Co., Ltd. Gordon and Breach Science Publishers Office of Naval Research National Science Foundation Crystaloid Electronics Minolta, Ltd. Society for Information Display Blake Industries EM Industries, Inc. Instec. Inc. Linkam Scientific Instruments ROLIC, Ltd. Siemens Energy and Automation, Inc. Aerospace Display Systems and McNeil Travel

\*NSF Science and Technology Center for Advanced Liquid Crystalline Optical Materials
A Consortium of Kent State University, Case Western Reserve University, and University of Akron

# The 16th International Liquid Crystal Conference

June 24-28, 1996

#### Conference Chairman

#### Satyen Kumar, Kent State University, USA

#### International Advisory Committee

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S. Zumer (Slovenia).

#### 16th ILCC

June 24-28, 1996 Kent State University Kent, Ohio, USA

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Honorary Chairman:

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Chairman:

S. Kumar

Vice-Chairman:

Secretary:

J.L. West D. Finotello

Treasurer:

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J.L. Koenig

A.J. McKinney

O.D. Lavrentovich

A.A. Mihalus

J.W. McCargar

#### CONFERENCE ADDRESS

#### **MESSAGE BOARD**

Lecture site:

Kent State University Student Center (KSC)

Kent State University

Kent, OH 44242-0001, USA

Phone: (330) 672-7770

Fax: (330) 672-2796

E-Mail: ILCC16@alice.kent.edu

Outside Ballroom Second Floor, KSC

## INTERNATIONAL LIQUID CRYSTAL CONFERENCES

Conference	Year	Place	Number of Papers
First	1965	Kent, Ohio, USA	42
Second	1968	Kent, Ohio, USA	78
Third	1970	Berlin, Germany	115
Fourth	1972	Kent, Ohio, USA	181
Fifth	1974	Stockholm, Sweden	260
Sixth	1976	Kent, Ohio, USA	271
Seventh	1978	Bordeaux, France	296
Eighth	1980	Tokyo, Japan	371
Ninth	1982	Bangalore, India	354
Tenth	1984	York, UK	430
11th	1986	Berkeley, California, USA	539
12th	1988	Freiburg, Germany	503
13th	1990	Vancouver, Canada	715
14th	1992	Pisa, Italy	956
15th	1994	Budapest, Hungary	944
16th	1996	Kent, Ohio, USA	900
17th	1998	Strasbourg, France	
18th	2000	Japan	

#### Welcome

The members of the Organizing Committee welcome more than six hundred participants from all over the world to Kent State University. It is our sincere hope that at this conference in Kent, away from the distractions of a cosmopolitan city, the participants will be able to concentrate on the scientific and technological advances in the field of liquid crystals. We also tried to create attractive distractions in the form of evening social programs and the conference banquet.

The organizers have looked forward to the conference with a sense of anticipation since it was awarded to Kent State University three years ago. During the past year, anticipation was increasingly mixed with a sense of dread at the thought of this monumental task. One of the things that sustained us was a phrase from somewhere, "If Alexander the Great can do it, we can do it!" You, the conference participants, will determine how well we have done it.

The organizers strived to make the best possible arrangements at a reasonable cost. The conference facilities are second to none in their utility and comfort. On-campus accommodations in dormitories present a cost-effective alternative to expensive hotels.

We are indebted to the sponsors of the conference. Their generous donations permitted us to give financial aid in the form of registration fee waivers to nearly one hundred scientists, including plenary speakers, invited speakers, and financially disadvantaged scientists, without any cost to the participants. In keeping with the wishes of our sponsors, this aid was given to needy students, postdocs, junior faculty, and senior faculty, in that order of priority. No member of the Organizing Committee nor anyone from Kent State University was exempted from the registration fee. We regret, however, that many deserving members of the liquid crystal community were unable to attend the conference due, at least in part, to lack of support.

We arranged two short courses at a nominal cost for the benefit of new and curious members in the liquid crystal field. The short courses appear to be a successful addition in spite of being a new element to the ILCCs.

We believe that we have a very exciting conference because of the caliber of the presentations. Every participant has spent time and effort in preparing for this conference. We hope that it proves to be personally and scientifically beneficial to all.

Satyen Kumar Chairman 16th ILCC

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Kent State University CampusB	ack Cover

#### 16TH ILCC

The International Liquid Crystal Conference provides a forum for the exchange of scientific ideas and technological advances in every aspect of liquid crystal research. The conference program consists of plenary, invited, and contributed talks and poster presentations.

The first International Liquid Crystal Conference (ILCC), which attracted about 50 scientists, was organized by Professor Glenn H. Brown at Kent State University in 1965. It has since been held in ten countries and meets on a biannual basis with an increasing number of presentations and participants. The 16th International Liquid Crystal Conference returns to its birth place after 20 years. It will be held at the Kent Student Center and is organized by the Departments of Physics and Chemistry and the Liquid Crystal Institute of Kent State University. The number of presentations at the 16th ILCC is expected to be nearly 900.

The Conference organizers are thankful to the sponsors. Their generous donations made it possible to keep the registration fees low and to provide fee waivers to scientists from financially disadvantaged countries.

#### Conference Site

The conference site, Kent State University, today has the unique distinction of being the largest center for liquid crystal research in the world. Liquid crystal research at Kent became streamlined and well focused in 1965 when Prof. Glenn H. Brown founded the Liquid Crystal Institute. Joined by J.W. Doane, D.L. Johnson, D.L. Uhrich, N. Spielberg, E. Gelerinter, and A. Saupe of the Department of Physics and M.E. Neubert, A. deVries, and J.L. Fergason of the Liquid Crystal Institute, it quickly gained international recognition and the reputation of being a center of excellence. It is the site of numerous scientific discoveries and inventions.

Liquid crystal research at Kent took a new direction with the establishment of the National Science Foundation Science and Technology Center for Advanced Liquid Crystalline Optical Materials (ALCOM) under the directorship of J.W. Doane, one of the inventors of polymer dispersed liquid crystal (PDLC) technology. ALCOM makes it possible for more than 30 scientists from Kent, Case Western Reserve University, and the University of Akron to collaborate. Scientists working on liquid crystals at Kent State University include D.W. Allender, J.W. Doane, D. Finotello, S. Kumar, and S.N. Sprunt from the Department of Physics, J.E. Fulghum from Chemistry, P.A. Farrell, E.C. Gartland, Jr., and A. Ruttan from Mathematics and Computer Science; and P.J. Bos, L.-C. Chien, J.R. Kelly, O.D. Lavrentovich, M.E. Neubert, P. Palffy-Muhoray, J.L. West, and D.-K. Yang from the Liquid Crystal Institute.

#### **Conference Proceedings**

The proceedings of the conference will be published in special volumes of *Molecular Crystals* and *Liquid Crystals*. All registered participants will received a complimentary copy of the proceedings and 50 free reprints of their contribution. Camera ready manuscripts are due at the time of the conference. Manuscripts will be collected by a representative of Gordon and Breach near the registration desk during registration hours. The manuscripts will be peer reviewed and subjected to the same high standards as in a normal publication process.

#### **Pre-conference Short-Courses**

In addition to the normal program of the conference, two short courses, *Liquid Crystal Applications* and *Physical Characterization of Liquid Crystal*, were held on Sunday, June 23. Participants attemded lectures by prominent scientists and received bound lecture notes. The lecturers and topics of the tutorials are listed below.

#### Liquid Crystal Applications

<u>Speaker</u>	<u>Topic</u>
N.A. Clark	Ferroelectric displays
T. Scheffer	Supertwisted nematic (SN) displays
P.J. Bos	Twisted nematic (TN) displays
P.S. Drzaic	Polymer liquid crystal composites (NCAP, PDLC)
J.L. West	Polymer and surface stabilized cholesteric displays

#### Physical Characterization of Liquid Crystals

Speaker	<u>Topic</u>
P. Barois (France)	Liquid crystal ordering
S. Zumer (Slovenia)	Macroscopic description of liquid crystals
A.M. Levelut (France)	X-ray characterization of liquid crystals
C. Zannoni (Italy)	Computer simulations of liquid crystals
M.A. Anisimov (Russia/USA)	Phase transitions and critical phenomena in LCs

#### Registration

Conference registration includes admission to all lectures, conference packet (Program and Abstract book, etc.), admission to social activities, and one set of conference proceedings. Registration fees for accompanying persons include admission to all social activities open to conferees. Payment may be made by Visa or Master Card, traveler's checks, or cash at the onsite rates:

Status	Registration Fee
ILCS Member	US \$ 450
Non-Member	475
Student	325
Accompanying Person	125

#### On-site registration schedule:

Sunday June 23 1400 - 2200; KSC second floor Mon - Wed June 24-26 0800 - 1500; KSC second floor

#### **Presentations**

Only registered participants have the right to present a paper and to participate in the 16th ILCC. The official language of the conference is English.

All speakers are requested to present themselves to the session chairperson at least five minutes before the session. Standard 35 mm slide and overhead projectors will be available for oral presentations. Special equipment, such as a video system, will be provided only to those who requested it on the abstract submission form. Slides should be loaded in trays and given to the audio-visual technician before the beginning of the session. They should be collected at the end of the session.

The conference program features five plenary lectures (50 minutes with 10 minute discussion), 37 invited (25/5 minutes), 84 contributed (15/5 minutes) lectures, four Glenn Brown Award lectures, and three "in memoriam" talks. There will be three parallel sessions.

The poster boards are approximately 80cm (width) x 120cm (height). Two poster sessions will be held in parallel and will last 1 hour 45 minutes. Presenters must be near their posters during the scheduled time. Posters must be removed at the end of each session or they will be removed by the organizers and may be difficult to find at a later time. Authors with "standby" (late submission) posters should inquire at the conference desk for space availability. These poster presentations have been assigned numbers ending with an "S".

#### **Industrial Exhibition**

An exhibition showcasing the products of publishers in the liquid crystal field and manufacturers of liquid crystal materials, display devices, test and measurement instrumentation, and electrooptical equipment will be held June 25-27 in room 206 of the Kent Student Center (KSC). The following companies will have their products on display:

Blake Industries
Crystaloid Electronics
Instec, Incorporated
IO Graphics, Inc.
Linkam Scientific Instruments
Minolta, Ltd.
Novocontrol
Siemens Energy and Automation, Inc.
Society for Information Display
Springer Verlag
Taylor and Francis
The Royal Society of Chemistry

#### Official Airlines and Travel Agent

Continental Airlines is the official airline of the 16th ILCC. Use reference code IRKFZ1 when making reservations to obtain the conference rates. For domestic travel you will receive 5% off discounted fares or 45% off regular fares. For international travel, the discount will range from 5 to 45%, depending on the embarkation point. For conference rates on car rental, call AVIS at 1-800-331-1600 and use reference code J625310.

McNeil Travel Service [phone (330) 678-8890, fax (330) 678-0655], the official travel agent for the conference, is prepared to assist conference attendees in making their travel arrangements and reconfirming reservations.

#### **Local Transportation**

Free transportation between Cleveland Hopkins International Airport and Kent will be provided according to the schedule given below.

Leave Airport:

SAT June 22:

1300, 1600, 1900, and 2230 hrs

SUN June 23:

1100, 1400, 1700, 1900, 2000, 2130, 2230, and 2330 hrs

Leave Kent:

FRI June 28:

1200, 1300, 1400, 1500, 1600, 1800, 1900, 2100 hrs

SAT June 29:

0800, 1030, 1300 hrs

Without a reservation, space will be subject to availability and allocated on "first-come first-served" basis. You may also arrange transportation by calling Laura's Transportation Service (800-206-6961) or Irv Nichols (330-655-4392); confirm your cost when you call.

Participants staying in off-campus local motels (see Accommodations) will be transported to/from the conference site free of charge. Participants staying in off-site motels must arrange their own transportation.

#### Meals

No meals are covered by conference registration fees. The conference provides only refreshments and beverages during the oral sessions and coffee breaks.

Continental breakfast is included in the cost of on-campus housing. A self-serve breakfast station can be found in the lobby of your dormitory. Those staying off campus will find several restaurants in the vicinity of their motel. Please ask the main desk at your motel for details.

You may purchase meals at the Food Court (Arabica, Aunt Chilada's, Friendly's, Hot Sam's, Mamma Ilardo's, Mark Pi's, McDonald's, and Subway) located on the first floor of the Kent Student Center. Also available in the Kent Student Center are the Schwebel Garden Room (3<sup>rd</sup> floor; reservations required; call 672-2583; closed Monday) and the A la Carte Cafeteria (2<sup>nd</sup> floor KSC).

Conference buses (free of charge) will run frequently between downtown Kent and the Kent Student Center to take participants to local restaurants during lunch and dinner times. Your conference badge will serve as the bus pass.

#### **Currency Exchange and Banking**

Only US dollars are accepted by local merchants and by the conference. Credit cards and traveler's checks are widely accepted. The Kent State branch of Bank One, located in the Student Center, has agreed to make special arrangements for limited currency exchange service for the convenience of conference participants.

#### List of Participants

Participants are requested to check their address, telephone number, and e-mail address for accuracy in the draft list of participants before Tuesday at 1400 hrs. A final list will be available at the registration desk on Thursday.

#### **Social Activities**

Participation in the following social activities requires conference or accompanying persons registration. You may purchase extra tickets at the cost indicated subject to availability. For activities included in the registration, your conference badge will serve as your ticket.

Necestion Sunday, June 25 Included in registration	Reception	Sunday, June 23	Included in registration
--	-----------	-----------------	--------------------------

1900-2200 hrs

KSC Ball Room \$30 for extra tickets

Cash Bar and Mon, Tues, Thu nights
Social Mixer June 24, 25, and 27

2000 - 2300 hrs

Rathskeller, KSC (Basement) \$10 for extra tickets

Comedy Show Midwest Comedy Tool and Die Included in registration

Monday, June 24

1900 - 2000 and 2100 - 2200 hrs Rathskeller, KSC (Basement)

Play Driving Miss Daisy \$15

Tuesday, June 25 2100 - 2300 hrs

Porthouse Theater

Buses leave KSC at 2015 hrs

Conference Banquet Wednesday, June 26 Included in registration

at Sea World \$50 for extra tickets

1830 - 2100 hrs Buses leave KSC 1530 hrs

Concert Bachmann-Klibonoff-Fridman Trio Included in registration

Thursday, June 27 Limited space; first come-first seated

2000 - 2200 hrs \$15 for extra tickets Kiva, KSC

Barbecue Farewell Friday, June 28 \$10

Lunch KSC Plaza
1240 hrs

#### **Accompanying Persons Program**

These activities will take place during the hours of the conference and are open to registered conferees or accompanying persons. This program is in addition to the *Social Activities*. The organizers reserve the right to cancel an activity which is under-subscribed.

#### Monday, June 24, Shopping Trip, 0930-1630 hours; Transportation \$10

Day-long excursion to Aurora Farms Factory Outlet Mall in Aurora, Ohio. The 64 shops offer a wide range of merchandise from major manufacturers at substantially discounted prices. Participants will receive a book of discount coupons, courtesy of the Aurora Farms vendors. The mall setting resembles an Early American village. Lunch is available in an on-site restaurant or in a food court.

Tuesday, June 25, Rock and Roll Hall of Fame, Cleveland, Ohio, 0930-1600 hours Transportation and admission: \$20

The unique museum, featuring the legends of rock and roll music, opened in fall 1995 to rave reviews. The building, designed by renowned architect I.M. Pei, is located on the Lake Erie shore, within walking distance of downtown Cleveland. The trip allows time to view the museum exhibits and explore part of the city. Lunch is available in the museum or in The Galleria at East 9th Street.

Wednesday, June 26 or Friday, June 28, Kent State University Museum, Hours: 1000-1645 Suggested activity, at your convenience; walking distance, \$3.00 donation

Located on the campus at the corner of Main and South Lincoln Streets, the KSU Museum features an international collection of period and designer costumes and an extensive exhibit of American art glass.

Thursday, June 27, Amish Country Tour, Holmes County, Ohio, 0830-1600 hours Transportation, ticket to Mennonite Information Center exhibit, lunch: \$30.00

Day-long excursion to the area of Ohio which is home to Amish and Mennonite farmers; both groups trace their religious and cultural heritage to events in Zurich, Switzerland, in 1525. Their settlements moved westward with the expansion of the United States and the largest population is located in east-central Ohio. The trip will include a visit to Lehmann's Hardware in Kidron, a historical overview at Berlin, and lunch at an Amish restaurant, Der Dutchman in Walnut Creek.

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#### **SCHEDULE OF EVENTS**

## Sunday, June 23, 1996 Kent Student Center

			Short Courses				
			Physical Characterization of Liquid Crystal Applications Organizer: Lavrentovich Organizer: Kelly				
10:00 -	12:00		Lectures Room 306	Lectures Governance Chambers			
12:00 -	14:00		Lunch (not included)				
14:00 -	17:00	Registration Second Floor	Lectures Lectures Room 306 Governance Chamber				
17:00 -	19:00		Dinner (not included)				
19:00 -	22:00		Reception Ballroom				

# Comedy requires proper tools



Members of Midwest Comedy Tool & Die Perform on Monday at 19:00 and 21:00 at Rathskeller

In the cerebral fast lane of "Jeopardy!" only the quick-witted survive. Especially when the categories are yanked out of thin air.

You've got to be fast with the buzzer. The pressure's always on, the stakes always high. The rewards? Well... you can always gloat to your friends.

OK, ready? Here we go. The category is "famous people."

Answer: Bob Marley.

Buzzzz: Who's so high he doesn't know he's

Yes! That's correct for \$100. Next answer, please.

Answer: Forrest Gump.

Buzzzz: Who was Rainman... with better luck?

That's right! Next answer, please.

Answer: O. J. Simpson.

Buzzzz: Who should have grabbed a hertz rent-a-car and gotten the hell out of Dodge?

Yes! We have a new winner: The Midwest Comedy Tool & Die, a deranged flock of young comics who play "Jeopardy!" the same way they play everything else: off the cuff and wildly funny.

The group, from Columbus, Ohio, features seven members, although only five tour together at one time ("the van only holds five"). They're a witty assortment of writers, musicians, comics and actors who rely on audience participation to fill out their home-grown blend of theater, comedy and music. They range in age from 21 to 43

"The crowd really writes the show," said Roberts, who does a wickedly funny impersonation of Don Knotts. The troupe uses suggestions from the audience to stretch their sketches in surprising directions. For example, a skit about starving ferrets revolved around Mick Jagger, Bob Dylan and a Scottish veterinarian who looks like "Bud Bundy with tapeworm."

You'll also get a kick from the troupe's "freeze tag" routine, in which the comics constantly replace one another, turning creative conversations into risible repartee.

It's like watching "Saturday Night Live" live. Only funnier.

# Monday, June 24, 1996

08:00	-	08:30	Opening Ceremony Chair: KUMAR Ballroom					
08:30	_	09:30	Plenary	Field Induced Orde	er and Reversible Entr	opic		
				Thermal Effects in	Liquid Crystals			
İ				Durand				
			Chair	DOANE				
09:30	-	10:00			Coffee			
			Session	A1: Free Surfaces and Interfaces	A2: Theory and Computer Simulations	A3: Biological and Lyotropic Systems		
			Room	Ballroom	Kiva	KSC 306		
			Chair	SHASHIDHAR	PASINI	KELLY		
10:00	-	10:30	Invited	Saupe	Fournier	Kamien		
10:30	-	11:00	Invited	Meister	Selinger	Nounesis		
11:00	-	11:20		Golemme	Zannoni	Hendrikx		
11:20	_	11:40		Buka	Memmer	Westerman Kothe		
11:40	-	12:00			Musevic Lukac  Martinez-Miranda Glaser			
12:00	-	12:20		Martinez-Miranda	Amaral			
12:20	-	13:45		Lunch (not included)				
12.45		15.20	Domes	AlP	A2P			
13:45	-	15:30	Posters	Room 204-	illroom Balcony			
15:30	-	15:45		Coffee				
			Session	A1: Synthesis A2: Polymeric Liquid		A3: Optical Properties		
			<b>D</b>	Ballroom	Crystal Systems			
			Room Chair	NEUBERT	Kiva SCHADT	KSC 306 KOBAYASHI		
15:45		16:15	Chan	Yu	Kitzerow	Klittnick		
13.43	_	10.15		(Invited)	(Invited)	Li (16:05)		
16:15	_	16:35		Bezborodov	Mehl	Galabova (16:25)		
16:35	_			Kaszynski				
16:55	_	17:15		Hird	Bai	Hasegawa (17:05)		
17:15	-	17:35		Tschierske				
17:35	-	19:00	***	Dinner (not included)				
19:00	-	20:00			nedy Show athskeller			
21:00	-	22:00		Comedy Show (Repeat Performance) Rathskeller Cash Bar				
	-	23:00						



# PORTHOUSE THEATRE COMPANY

presents



Added performance arranged on behalf of the 16th International Liquid Crystal Conference Tuesday, June 25, 1996

21:00 Curtain

Tickets still available. Inquire.

••• PROFESSIONAL SUMMER THEATRE AT BLOSSOM MUSIC CENTER •••
1145 West Steels Corners Road, Cuyahoga Falls, Ohio

This Pulitzer Prize-winning play, which went on to become an Academy Award-winning movie, tells the heart warming and gently humorous story of the unlikely relationship between an aging, crotchety Southern Lady and the proud, soft spoken black man who, in time, becomes her best friend.

"Gives off a warm glow of humane affirmation"-Variety
"A total delight...Worth the drive from anywhere!"-N.Y. Daily News

# Tuesday, June 25, 1996

08:00	-	09:00	Plenary	Liquid Crystal Devices and Devices for Liquid Crystals  Patel Ballroom LOWE				
09:00	_	09:20			Cof	ffee		
			Session  Room Chair	B1: Polymer B2: Molecu Dispersed Liquid Organization in Crystals Materials Ballroom Kiva		n in Novel C ials a	B3: Non-Linear Optical Phenomena  KSC 306 SINGER	
09:20	_	09:50	Invited	YANG Sluckin	UCHI Franceso		Fontana	
09:50		10:20	Invited	Drzaic	El Al		Walba	
			Invited	Chien	Dietzn		Herman	
10:20 10:40	-	10:40		Aphonin	Smi		Kosa	
11:00		11:20		Bata	Che		Kreuzer	
11:20	_	11:40		Mulder	Schmid			
11:40	-	13:00	*	Lunch (not included)				
13:00	-	14:45	Posters	B1P B2P Room 204-206 Ballroom Balcony				
14:45	-	15:00		Coffee				
15:00	-	15:30	Richard Horns					
15:30	•	16:45		Brown Awards Ballroom ERWALL				
16:45	-	17:00		Coffee				
16:45	-	18:45	Posters			B4P om Balcony		
18:45	-	20:15	X		Dinner (no	t included)		
21:00	•	23:00	( ) ( )	Play at Porthouse Theatre "Driving Miss Daisy"  Buses leave from KSC at 20:15; return at 23:30  Social Mixer Cash Bar Rathskeller			Cash Bar	

# Sea World

1-800-63-SHAMU



# Wednesday, June 26, 1996

08:00	-	09:00	Plenary Chair	Shapes and Dynamics of Giant Vesicles Seifert Ballroom BLINC				
09:00	-	09:20		Coffee				
			Session Room Chair	C1: Alignment at Interfaces Ballroom TREBIN	C2: Ferroelectrics  Kiva  CLARK	C3: Elasticity  KSC 306  LAVRENTOVICH		
09:20	-	09:50	Invited	Barberi	Bahr	Singh		
09:50	-	10:20	Invited	Zhuang	Glogarova	Pergamenshchik		
10:20	_	10:40		Raja	Jakli	Evangelista		
10:40		11:00		Wu	Lubensky	Kapanowski		
11:00		11:20		Brown	Takezoe	Yokoyama		
11:20	_	11:40		Haslam	Vij	Kiselev		
11:40	-	12:20		ILCS General Meeting Ballroom				
12:20	-	13:45	***	Lunch (not included)				
13:45	•	15:30	Posters	C1P Room 204-206	C2P  Ballroom Balcony	C4: Education Outreach KSC 306		
10.45		14.05			· ·	Chair: MARROUM		
13:45		14:05				Darling Marroum		
14:05		14:25				Martinez-Miranda		
14:25		14:45				Domingo Domingo		
14:45 15:05		15:05 15:25				Graff		
15:30		17:30		Buses to Sea World				
18:30	-	20:30		Conference Banquet				
21:00	-	23:00		Return to Kent State University from Sea World				



Maria Bachmann, violin
"A violinist of soul and
patrician refinement. ... [She
has] the strength, agility and
precision that we have come
to expect from a modern
violinist, yet her playing has
an affecting warmth that is
distinctly unusual."

Jon Klibonoff, piano
"Technically and interpretively, all was in place.
Contrapuntal lines were crisp and well balanced, tempo relationships had an inherent rightness, and [his] deft use of dynamics gave the rendering color and dimension."

Semyon Fridman, cello
"He manipulated the music's
emotional flow in a subtle,
masterly way. ... A moving
balance of delicacy and
power."
THE NEW YORK TIMES

ONCERTARTISTS GUILD

Performance: Thursday, June 27, 1996; 20:00

Kiva, Kent Student Center

# Thursday, June 27, 1996

08:00	-	09:00	Plenary Chair	Liquid Crystal Sma Meyer Ballroom CLADIS	art Reflectors	3		
09:00	_	09:20			Con	ffee		
			Session	D1: Phase Transition in Bulk	D2: For Antiferroelec		D3: Optical Properties of Chiral Liquid	
			Room Chair	Liquid Crystals Ballroom DE JEU	Kiv TAYI	a	Crystals KSC 306 LUBENSKY	
09:20	-	09:50	Invited	Garland	Le	е	Suresh	
09:50	-	10:20	Invited	Iannacchione	Photi	nos	Longa	
10:20	-	10:40		Caerels	Rosen	blatt	Galatola	
10:40	-	11:00		Yethiraj	Pana	rin	Radley	
11:00	-	11:20		Sonntag	Blir	ıc	Moriya	
11:20	-	11:40		Collings Pozhidaev			Kruerke	
11:40	-	13:00	X	Lunch (not included)				
13:00	-	14:45	Posters	D1P Room 204-206 Bal			D2P Ilroom Balcony	
14:45	-	15:10		Coffee				
			Session	D1: Liquid Crystals D2: Reorientational In Restricted Dynamics			D3: Liquid Crystals Under Shear Flow	
:			Room Chair	Geometries Ballroom Kiva COLLINGS PALFFY-MUHORAY			KSC 306 ROSENBLATT	
15:10	-	15:40	Invited	Crooker	Santar	nato	Mang	
15:40	_	16:10		Deeg	Tori	ımi	Martins	
				(Invited) (Invited)		Borzsonyi		
16:10	-	16:30		Sinha Morse			Noirez	
16:30	-	16:45		Coffee				
16:45	-	18:30	Posters	D3P			D4P	
			•0	Room 204-	206	Ba	llroom Balcony	
18:30	-	20:00			Dinner (no	t included)		
20:00	-	22:00		Concert Bachmann-Klibonoff-Fridman Trio Kiva Social Mixer Cash Bar				
	+	23:00		Rathskeller				

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Friday, June 28, 1996

08:30	-	09:30	Plenary	Microconfined Liquid Crystals		
			Ob.:	Zumer		
			Chair	Ballroom		
09:30		10:00		ANISIMOV	Coffee	
09.30		10.00	<u> </u>	Confee		
			Session	E1: Phase Transitions	E2: Ferroelectric	E3: Orientational
				in Thin Films	Devices	Order and Dynamics
			Room	Ballroom	Kiva	KSC 306
			Chair	BROCK	BOS	KHETRAPAL
10:00	-	10:30	Invited	Stoebe	Fukuda	Ramanathan
10:30	-	11:00	Invited	Mol	Mochizuki	Veracini
11:00	-	11:20		Bechhoefer	Guymon	Tansho
11:20	-	11:40		Van Winkle	Huang	Dong
11:40	-	12:00		Demikhov	Mitov	Crain
12:00	-	12:20		Chou	Milburn	Terzis
12:20	-	12:40			Closing Ceremony Ballroom	
12:40					Barbecue Lunch KSC Plaza	

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#### Dr. Glenn H. Brown: Pioneer in Liquid Crystal Research

Dr. Glenn H. Brown, founder of Kent State University's Liquid Crystal Institute died April 18, 1995, at the age of 79.

Dr. Brown, a Regents Professor and Professor Emeritus in the Department of Chemistry, established the Institute and the International Liquid Crystal Conference in 1965. He served as Institute Director until 1983; he retired in 1985. He also served as Chair of the Department of Chemistry and as Dean for Research. The Liquid Crystal Institute, the first and largest academic center in the United States devoted to basic and applied research on liquid crystals, was named in his honor by the Kent State University Board of Trustees in 1986. The Planning and Steering Committee of ILCCs instituted the Glenn Brown Award in 1986 for outstanding dissertation research in physics, chemistry, and applications of liquid crystals.

Dr. Brown's article published in *Chemical Reviews* (1957), which he co-authored with W.G. Shaw, sparked an international resurgence in liquid crystal research. As an internationally recognized authority in his field, he edited six volumes of *Advances in Liquid Crystals* (Academic Press) and served as editor and editor-in-chief of *Molecular Crystals and Liquid Crystals* (Gordon and Breach). He received numerous awards, including the Kent State University President's Medal (1980), Governor's Excellence Award (1986), Brinkman Award (1981), and the Morley Award (1977). He had affiliations with a large number of professional and honor societies and served several of them in an official capacity.

Dr. Brown was born in Logan, Ohio, in 1915; he received his Bachelor's degree from Ohio University in Athens (1939); Master of Science degree from Ohio State University (1941); and Ph.D. from Iowa State University (1951). His wife, Mrs. Jessie A. Brown, remains an active member of the liquid crystal community.

#### Dr. Richard M. Hornreich: Noted Theorist on Phase Transitions

Richard Hornreich, distinguished physicist in the Department of Complex Systems at the Weizmann Institute of Science in Rehovot, Israel, and a leading theorist on cholesteric and blue phases of liquid crystals, died of a heart attack on October 24, 1994; he was 56. He is survived by his wife Geraldine, two daughters, a son, two granddaughters, and his mother.

Dick (as he was known to his friends and colleagues) grew up in the Bronx section of New York City before earning B.Sc., M.Sc., and E.E. degrees in Electrical Engineering from Massachusetts Institute of Technology. After two years with LFE corporation in Boston, he returned to graduate school at the Weizmann Institute and obtained his Ph. D. degree in Physics in 1967.

Following three years with GTE Corporation, he accepted a faculty position at the Weizmann Institute that he held for 24 years. He spent sabbatical leaves at Yale University and Imperial College, London. He served in several administrative capacities including Dean of the Feinberg Graduate School and Chairman of his Department at the Weizmann Institute. He established collegial research efforts with many physicists, most notably Professor S. Shtrikman, and directed numerous students. He was honored with the Leedy Memorial Award in 1972 for his work on the magnetoelectric effect and was a member of the American Physical Society, the Israel Physical Society, Sigma Xi, and the IEEE.

Dick's research interests covered a wide range of topics in condensed matter physics where he consistently made ground-breaking contributions. From work on magnetic systems and phase transitions early in his career, he developed the beautiful and elegant theory of the Lifshitz point, which has been successfully used in nematic and smectic liquid crystals. Always interested in the mechanism for the onset of periodic structure, he pioneered in developing models of the cholesteric phase and the blue phases of liquid crystals. Critical phenomena, melting in reduced dimensionality, the existence of photonic band gaps in structures of specific symmetry, and boundary layer order transitions in nematogenic systems were all problems of interest to him.

#### Dr. David L. Johnson: Creative Researcher and Teacher

David L. Johnson, Professor of Physics at Kent State University, died on December 30, 1995, at age 59, of cancer. He is survived by his wife Rosine, a son, and a daughter. Dr. Johnson received his Bachelor's degree from St. Olaf College in 1960 and Ph.D. in superconductivity from Iowa State University in 1966.

He joined the faculty of Kent State University nearly thirty years ago, in 1966, as an assistant professor. In 1972, he was named associate professor and was promoted to full professor in 1981. He held visiting appointments at the University of Hawaii, Massachusetts Institute of Technology, and the University of Washington. In addition, he was an active member of the American Physical Society, Sigma Pi Sigma, and Sigma Xi. His university activities were extensive as he served on the computer science curriculum committee, the academic and research challenge committees, college advisory committee, and various departmental committees. Dr. Johnson received a faculty research fellowship at Kent State University, a Case-Lewis Summer Faculty fellowship, and a NASA Lewis Research Center fellowship.

In the beginning of his career, Dr. Johnson studied thermal properties of superconducting materials; however, he devoted most of his research effort to the study of high-precision ac heat capacity and quasi-elastic light scattering of phase transitions in liquid crystals. He made several important contributions to this field, including the universality of nematic-smectic-A1 smectic-C phase diagram topology. Based on his accomplishments, he was awarded a National Science Foundation Creative Research Award. During his career Dr. Johnson directed thirteen Ph. D. dissertations and two Masters theses. He gave nearly ninety scholarly presentations and produced a large number of scientific publications. Dr. Johnson was instrumental in securing major research grants and fellowships totaling nearly five million dollars from various agencies including the National Science Foundation and NASA.

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#### LECTURE SCHEDULE

		CI OKE SCHEDULE	
Monda	y, June 24, 1996		
8:00	Opening Ceremony Chair: S. Kumar.	Location: Ballroom	
8:30	Plenary Lecture Chair: J.W. Doane Field Induced Order and R G. Durand	Location: Ballroom  eversible Entropic Thermal Effects in Lig	quid Crystals
9:30	Coffee		
	ee Surfaces and Interfaces air: R. Shashidhar	Location: Ballroom	
10:00	On the Topography of Free Surfa A. Saupe	ces of Liquid Crystals	Abstract No. A1.I01
10:30	The Free Surfaces of Cholesteric R. Meister	A1.I02	
11:00	Surface Interactions in PDLC Studied by Electric Field Synchronized NMR A. Golemme		
11:20	Comparison of Experimental and Phase Field Model Results on the Growth of Nematic-Smectic-B Interfaces  A. Buka		
11:40	Observation of Critical Forces in Force Microscope I. Musevic	A1.O05	
12:00	Time Evolution of the Structure of L.J. Martinez-Miranda	f Confined Smectic-C* Films	A1.006
	eory and Computer Simulation	Location: Kiva	
10:00	Recent Progress on Phase Bound J.B. Fournier	laries of Soft Matter	A2.I01
10:30	Theory of Chiral Instabilities in Smectic-A Liquid Crystals J.V. Selinger		
11:00	Computer Simulations of Polar Gay-Berne Systems C. Zannoni		
11:20	Computer Simulation of Chiral Liquid Crystal Phases - A Phase Diagram of the Chiral Gay-Berne Discogen  R. Memmer		
11:40	Demixing of Binary Liquid Crystals: A Simulation Study R. Lukac		
12:00	Computer-Aided Design of Ferroelectric Liquid Crystals  M.A. Glaser  A2.0		

	logical and Lyber opic Systems	ion: KSC 306	
Chair: J. Kelly			Abstract No.
10:00	Weak Chirality in Ordered DNA Phases R.D. Kamien		A3.I01
10:30	Melting of Phospholipid Tubules G. Nounesis		A3.I02
11:00	Model Proposed for the Cubic Phase Identified in a Te System Y. Hendrikx	ernary Lyotropic	A3.O03
11:20	Physicochemical Characterization of Liquid Crystallin Bile and Lipid Digestive Mixtures P. Westerman	ne Phases in Model	A3.O04
11:40	Director Fluctuations and Viscoelastic Properties in E Effect of Cholesterol and Proteins G. Kothe	liomembranes: The	A3.O05
12:00	Micellar Changes at H- $N_c$ and $N_c$ - $N_{bx}$ - $N_d$ Phase Trans Liquid Crystals L.Q. Amaral	itions in Lyotropic	A3.O06
12:20	Lunch		
13:45	Posters		
15:30	Coffee		
A1: Syn	ion: Ballroom		
15:45	Mesogenic Behaviors of 4-Carboxy- and 4-Propenoxy. Stilbazolyl Esters L.J. Yu	-benzo-15-crown-5	A1.I07
16:15	Present and Future of the Liquid Crystals Chemistry V.S. Bezborodov		A1.008
16:35	Liquid Crystals Containing Boron Clusters: Design, S. Properties P. Kaszynski	ynthesis and	A1.O09
16:55	Heterocyclic Esters Exhibiting Frustrated Liquid Crys M. Hird	stal Phases	A1.O10
17:15	Liquid Crystalline Carbohydrates Forming Smectic, C Mesophases C. Tschierske	Columnar and Cubic	A1.O11
Sp	ymeric Liquid Crystal Systems  Locat onsored by the U.S. Office of Naval Research air: M. Schadt	tion: Kiva	
15:45	Polymer-Dispersed and Polymer-Stabilized Liquid Cry on Antiferroelectric and Chiral Discotic Systems HS. Kitzerow	ystals: Recent Results	A2.I07

#### Lecture Schedule Monday, June 24, 1996

		Abstract No.
16:15	Monodisperse Oligimeric Liquid Crystal Supermolecules with Defined Topology G.H. Mehl	A2.O08
16:35	Ferroelectric Properties of Novel Cyclic Siloxane Oligomers K. Grüneberg	A2.O09
16:55	Synthesis and Properties of Regiocontrolled Chiral Liquid-Crystalline Polyesters F. Bai	A2.O10
17:15	Optical Studies of Anisotropic Networks in Polymer Stabilized Liquid Crystals C.M. Hudson	A2.011
	nair: S. Kobayashi  Location: KSC 306	
15:55	Optically Induced Director Orientation in Dye Doped Liquid Crystals A.F. Klittnick	A3.I07
16:15	Azimuthal Surface Anchoring Energy in Photo-Induced PVCi Optical Anisotropic Alignment Films X.T. Li	A3.O08
16:35	Orientation and Surface Anchoring of Nematic Liquid Crystals on Linearly Polymerized Photopolymers H.G. Galabova	A3.O09
16:55	Competition of Self-Organization and Photo-orientation in LC Polymers J. Stumpe	A3.O10
17:15	Anchoring Energy at the Interface Between Optically Aligned Nematic LC and UV- Exposed Polyimide M. Hasegawa	A3.O11
17:25	Stabilization of Polymer Dispersed Liquid Crystals Using Surface Active Agents C. Sniveley	A3.O12

### Tuesday, June 25, 1996

	Tuesday, June	25, 1990	
8:00	Chair: A. Lowe	cation: Ballroom	
	Liquid Crystal Devices and Devices for Li J. Patel	quid Crystals	
9:00	Coffee		
	ymer Dispersed Liquid Crystals Loir: D. Yang	ecation: Ballroom	
9:20	Dielectric and Optical Properties in PDLC Films T.J. Sluckin		B1.I01
9:50	Some Effects of Anchoring on Droplet Structure an Polymer-Dispersed Liquid Crystal Materials P. Drzaic	d Device Properties in	B1.I02
10:20	Color Pixelization of Reflective Cholesteric Display LC. Chien	vs	B1.O03
10:40	Mechanisms of Orientational Ordering of Bipolar N Stretched PVA Matrix O.A. Aphonin	Vematic Drops in a	B1.O04
11:00	Infrared and Neutron Spectroscopy of Liquid Crysto L. Bata	al Composites	B1.O05
11:20	Modelling Structure Formation in Polymer-Dispers B.M. Mulder	ed Liquid Crystals	B1. <b>O</b> 06
	lecular Organization in Novel Materials Lo ir: T. Uchida	cation: Kiva	
9:20	Peculiar Macromolecular Organization in Nematic O. Francescangeli	: Poly(urethane-ester)s	B2.I01
9:50	Bowl-Shaped LCS at the Air Water Interface A. El Abed		B2.I02
10:20	Wedge-Shaped Molecules with Rigid Perfluorinate. E. Dietzmann	d Chains	B2.O03
10:40	Cholesteric Carbohydrate Liquid Crystals Incorpor Glucopyranose Moiety E. Smits	rating an Intact	B2.O04
11:00	Novel Glass-Forming Liquid Crystals: Molecular S.H. Chen	Design and Synthesis	B2.O05
11:20	Structural Investigation of Smectic Q Phase AM. Levelut		B2.O06
	n-Linear Optical Phenomena Lo ir: K. Singer	ocation: KSC 306	
9:20	Molecular Reorientations and Relaxation in Photos Birefringence and Polarized Micro-Raman Spectro M.P. Fontana		B3.I01

#### Lecture Schedule Tuesday, June 25, 1996

9:50	Ferroelectric Liquid Crystals for Second Order Nonline D.M. Walba	ear Optics	B3.I02
10:20	Light-Induced Molecular Reorientation and Change of Polarization in the Chiral Smectic A Phase  D. Hermann	Induced	B3.O03
10:40	Photoinduced Anisotropy in Dye-Doped Polymer Align T. Kosa	ment Layers	B3.O04
11:00	Anomalous Optical Kerr Effect in Dye-Doped Liquid C Isotropic Phase M. Kreuzer	rystals in the	B3.O05
11:20	Nonlinear Bleaching in the Selective Reflection of Non Nematic Liquid-Crystal Thin Films A. Schmid	-Absorbing Chiral	B3.O06
11:40	Lunch		
13:00	Posters		
14:45	Coffee		
15:10	Memorial Session Chair: A. Saupe	Location: Ballroom	

Glenn H. Brown: Pioneer in Liquid Crystal Research

J.W. Doane

Richard Hornreich: Noted Theorist on Phase Transitions

D. Allender

David Johnson: Creative Researcher and Teacher

P. Crooker

#### Glenn H. Brown Awards

Location: Ballroom

Chair: S. Lagerwall

#### Recipients:

Switching Columns: Electrooptic Effects with Columnar Liquid Crystals

Harald Bock, Free University, Berlin, Germany

Computational Modelling of Orientation and Flow Instabilities, Textures, Rheology, and Optics of Shearing Nematic Liquid Crystalline Materials

Won Hee Han, McGill University, Montreal, Canada

Study of the Electrooptical Characteristics of Amorphous and Multidomain TN-LCDs: A

Computer Simulation, Designing, and Experimental Verifications

Takashi Sugiyama, Tokyo University of Agriculture and Technology, Tokyo, Japan

Approaches to Spontaneously Polar Materials: Investigations of Bowlic Liquid Crystals Based on Calix[4] arenes

Bing Xu, University of Pennsylvania, USA

#### 16:45 **Posters**

### Wednesday, June 26, 1996

8:00	Plenary Lecture Chair: R. Blinc Shapes and Dynamics of Giant Vesicle U. Seifert	Location: Ballroom	
9:00	Coffee		
	gnment at Interfaces ir: H. Trebin	Location: Ballroom	Abstract No.
9:20	Aligning Effects in Nematics Due to Anchoring R. Barberi	Competition	C1.I01
9:50	Surface Induced Bulk Alignment of Nematic an X. Zhuang	d Smectic Liquid Crystal Films	C1.I02
10:20	Temperature Dependence of the Pretilt Angle of Liquid Crystal Aligned on Rubbed Side Chain I V.N. Raja	nd Polar Anchoring Strength of Nematic Liquid Crystalline Polymer	C1.O03
10:40	Effect of Chain Configuration on Bulk Liquid-(H.M. Wu	Crystal Alignment	C1.O04
11:00	Modelling Nematic Liquid Crystal Alignment of Grating Structures C. Brown	n Asymmetric Surface	C1.O05
11:20	The Nanometric Surface Structure of Substrate S.D. Haslan	s Used for Liquid Crystal Alignment	C1.O06
	roelectrics air: N. Clark	Location: Kiva	
9:20	Surface Transitions, Critical Adsorption, and S Inversion in Freely Suspended Films Ch. Bahr	Spontaneous Polarization	C2.I01
9:50	Spontaneous Periodic In-Layer Director Modu M. Glogarova	lations in Tilted Chiral Smectics	C2.I02
10:20	Ferroelectric Columnar Mesophases of Pyrami A. Jakli	idic Discotic Liquid Crystals	C2.O03
10:40	Chiral Fluctuations in Achiral Phases		C2.O04
11:00	T. Lubensky Distinct Ferroelectric Smectic Liquid Crystals Molecules with Banana Shape H. Takezoe	Consisting of Achiral	C2.O05
11:20	Dynamics of Collective Modes in Ferroelectric Confined Geometry J.K. Vij	: Liquid Crystals (FLCs) in	C2.O06
C3: Ela	sticity	Location: KSC 306	
	air: O. Lavrentovich		
9:20	Density Functional Theory for Elastic Constant Y. Singh	ts of Liquid Crystal	C3.I01

#### Lecture Schedule Wednesday, June 26, 1996

9:50	Elasticity Theory of a Spatially Restricted Nematic Liquid Crystal V. Pergamenshchik	C3.I02
10:20	Quadrupolar Interaction in Nematic Liquid Crystals  L.R. Evangelista	C3.O03
10:40	Elastic Constants of Binary Mixtures of Uniaxial Nematic Liquid Crystals  A. Kapanowski	C3.O04
11:00	Density Functional Theory of Surface-Like Elastic Constants H. Yokoyama	C3.O05
11:20	Freedericksz Transitions in a Planar Nematic Cell and the Surfacelike Elastic Constant Problem A.D. Kiselev	C3.O06
11:40	Lunch	
13:00	Posters	
	ucation Outreach air: R. Marroum	
		C4.O07
Ch	air: R. Marroum  Liquid Crystals in the Classroom	C4.O07 C4.O08
Ct 13:45	air: R. Marroum  Liquid Crystals in the Classroom  R. Darling  Liquid Crystals Outreach and Visual Aids	
Cr 13:45 14:05	Liquid Crystals in the Classroom R. Darling  Liquid Crystals Outreach and Visual Aids R. Marroum  From the Classroom to the Laboratory: A Way of Introducing Research	C4.O08

### Thursday, June 27, 1996

8:00	Plenary Lecture Chair: P. Cladis Liquid Crystal Smart Reflectors R. Meyer	)M	
9:00	Coffee		
	ase Transition in Bulk Liquid Crystals  Location: Ballroomir: W. De Jeu	m	Abstract No.
9:20	Static and Dynamic Critical Cp Behavior at Smectic-Hexatic Tran C. Garland	sitions	D1.I01
9:50	The Effect of Chirality on the Phase Transitions of Chiral/8CB Mi. G. Iannacchione	xtures	D1.I02
10:20	Photoacoustic and Photopyroelectric Measurements of the Thermo and Thermal Conductivity Anisotropy of Oriented Liquid Crystals J. Caerels	ıl Diffusivity	D1.O03
10:40	Real-Space Measurement of Nematic Director Fluctuations to Pro Nematic-Smectic-A Phase Transition A. Yethiraj	be the	D1.O04
11:00	Experimental Study of the Dynamic Properties of the N-SMA Phase P. Sonntag	e Transition	D1.O05
11:20	Unusual Short-Range Orientational Order in the Isotropic Phase of Smectogenic Liquid Crystals P.J. Collings	of Chiral	D1.006
	rroelectric and Antiferroelectric Phases Location: Kiva		
9:20	Layer Coupling for Molecular Orientation in the Field Induced Antiferroelectric-Ferroelectric Liquid Crystal Phase Transition S.D. Lee		D2.I01
9:50	Molecular Organization and Spontaneous Polarization in Smectics D.J. Photinos	5	D2.I02
10:20	Reversible Propagating Fingers in an Antiferroelectric Liquid Cry. C. Rosenblatt	stal	D2.O03
10:40	Investigation of Field Induced "Devil's Staircase" in AFLC by Hig Frequency Dielectric Spectroscopy Yu.P. Panarin	h-	D2.O04
11:00	Deuteron NMR of Ferroelectric and Antiferroelectric Liquid Cryst R. Blinc	'als	D2.O05
11:20	Surface Induced Transition from Antiferroelectric Phase to Ferroe Smectic C* One E.P. Pozhidaev	lectric	D2.O06

	tical Properties of Chiral Liquid Crystals Location: KSC 306 air: T. Lubensky	Abstract No.
9:20	Optics of Some Chiral Liquid Crystals K.A. Suresh	D3.I01
9:50	Nonlinear Dielectric Susceptibility in Blue Phases of Chiral Liquid Crystals L. Longa	D3.I02
10:20	Optical Activity of a Flexoelectrically-Deformed Small-Pitch Cholesteric Liquid Crystal P. Galatola	D3.O03
10:40	The Use of Decyl Esters of Amino Acid Hydrochlorides as Chiral Dopants in the Formation of Amphiphilic Cholesteric Liquid Crystals  K. Radley	D3.O04
11:00	Dielectric Relaxation in Dipole-Dipole Interaction System K. Moriya	D3.O05
11:20	Atomic Force Microscopy on the Free Surface of Frozen Discotic Cholesteric Blue Phases D. Kruerke	D3.O6
11:40	Lunch	
13:00	Posters	
	ir: P. Collings  Location: Ballroom	
15:10	Studies of Defects in Confined Liquid Crystals P.P. Crooker	D1.I07
15:40	Optical Kerr Effect Measurements of Orientational Dynamics of Cyanobiphenyls Confined to Nanoporous Random Matrices F.W. Deeg	D1.I08
16:10	Dielectric Relaxation of Nematic Liquid Crystals Confined in Porous Matrices G.P. Sinha	D1.009
	orientational Dynamics Location: Kiva ir: P. Palffy-Muhoray	
15:10	Optical Reorientation in Dye-Doped Nematics E. Santamato	D2.I07
15:40	Liquid Crystal Reorientational Dynamics: Recent Development of Time- Resolved FT-IR and Polarization-Modulated Ellipsometry H. Toriumi	D2.108
16:10	Time-Resolved X-ray Studies of Layer Behavior During Operation of a Ferroelectric Device A.S. Morse	D2.O09

#### Lecture Schedule Thursday, June 27, 1996

	quid Crystals Under Shear Flow  Location: KSC 306  air: C. Rosenblatt	Abstract No
15:10	Lyotropic Liquid Crystals Under Couette and Oscillatory Shear Flow J.T. Mang	D3.I07
15:40	Unusual Features of the Shear Viscosity Behaviour in Lyotropic Liquid Crystalline Polymers A.F. Martins	D3.O08
15:55	Shear Induced Instabilities in Nematics T. Börzsönyi	D3.O09
16:10	Shear Experiments on a Side-Chain Liquid Crystal Polymer: Determination of the Polymer Conformation and Liquid Crystal Structure  L. Noirez	D3.O10
16:30	Coffee	
16:45	Posters	

### Friday, June 28, 1996

8:30	Plenary Lecture Chair: M. Anisimov Microconfined Liquid Crystals S. Zumer	Location: Ballroom	
9:30	Coffee		
	se Transition in Thin Films ir: J. Brock	Location: Ballroom	Abstract No.
10:00	Calorimetric and Optical Reflectivity Studies of Liquid-Crystal Films T. Stoebe	of Thin Free-Standing	E1.I01
10:30	Fluctuations in Freely Suspended Smectic-A F E.A.L. Mol	ïlms	E1.I02
11:00	Temperature-Induced Orientational Transition Nematic Films J. Bechhoefer	ns in Freely Suspended	E1.O03
11:20	Nematic Bubbles in Freely Suspended Liquid (D.H. Van Winkle	Crystal Films	E1.004
11:40	Ferroelectricity in Free-Standing Films E.I. Demikhov		E1.O05
12:00	Scaling of Bond-Orientational Order Paramete Two-Dimensional Film C.F. Chou	ers in a 54COOBC	E1.006
	roelectric Devices ir: P. Bos	Location: Kiva	
10:00	Tilting Correlation in Adjacent Layers and Or Antiferroelectricity in Sm C*-like Liquid Crys A. Fukuda		E2.I01
10:30	Threshold Properties of SSFLC in Terms of Po A. Mochizuki	olarization Structures	E2.I02
11:00	Monomer Heterogeneity and Subsequent Phot Stabilized Ferroelectric Liquid Crystals C.A. Guymon	opolymerization of Polymer	E2.O03
11:20	Alignment of Ferroelectric Liquid Crystals in X. Huang	Polymer Network	E2.O04
11:40	Field-Induced Instabilities in Chiral Smectic I M. Mitov	LC Suppressed by a Polymeric Network	E2.O05
12:00	Aligned Ferroelectric Liquid Crystal/Polymer G.H.W. Milburn	Network Devices	E2.006

#### Lecture Schedule Friday, June 28, 1996

F3. Or	ientational Order and Dynamics Location: KSC 306	
	air: C. Khetrapal	Abstract No.
10:00	NMR in Liquid Crystals Spinning at and Near Magic Angle K.V. Ramanathan	E3.I01
10:30	Orientation, Structure and Dynamics in Highly Ordered Smectic Phases by <sup>2</sup> H NMR C.A. Veracini	E3.I02
11:00	Dynamic Mechanical and <sup>14</sup> N-NMR Studies on Structure of D-Phase M. Tansho	E3.O03
11:20	Detection of Second-Order Director Fluctuations by Deuteron Spin-Spin Relaxation at a Standard High Field R.Y. Dong	E3.O04
11:40	Vibrational Properties of Liquid Crystal Molecules J. Crain	E3.O05
12:00	Shape Dominated Ordering in Nematic Solvents. A Deuterium NMR Study of Cycloalkane Solutes A.F. Terzis	E3.006
12:20	Closing Ceremony Location: Ballroom	

### **Poster Presentations**

A1P	Nematic Modeling and Dynamics	39
A2P	Polymer and Elastomer Liquid Crystals  Sponsored by the Office of Naval Research	43
BIP	Polymer Dispersed/Stabilized Nematic and Cholesteric Liquid Crystals	47
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## FIELD INDUCED ORDER AND REVERSIBLE ENTROPIC THERMAL EFFECTS IN LIQUID CRYSTALS

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Electric fields can couple with the nematic orientational order parameter, and with the smectic one. Strong electric fields applied on the isotropic phase (I) of a nematogenic material can induce a nematic (N) phase [1] and a smectic phase [2]. The dynamical study of the I-N transition under field should show the reversible thermal entropic effect, well known in low temperature magnetic systems: when ordering by the field (or disordering) the orientational degree of freedom, entropy is transferred to (from) the other degrees of freedom, and the system should become heated (cooled). We optically observe the transient dynamics of the order S, on nematogenic 5CB, under pulsed AC electric field. Using S as a transient thermometer, we do observe reversible entropic heating and cooling [3], decreasing the "equilibrium" order when heating and creating metastable states when cooling. The effect is quantitatively described by a Landau-Khalatnikov model, with a fast adiabatic regime and a slow heat diffusion limited regime (thermal bottleneck) [4].

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- [3] I. Lelidis, G. Durand, Phys. Rev. Lett 76, 1868 (1996).
- [4] I. Lelidis, G. Durand, Festchrift for the 70th anniversary of Prof. Saupe, Gordon and Breach (to be published in 1996).

#### A1.I01

ON THE TOPOGRAPHY OF FREE SURFACES OF LIQUID CRYSTALS, A. Saupe, A. Hauser and M. Thieme, Max Planck Research Unit Liquid Crystalline Systems, Mühlpforte 1, D-06108 Halle/S., Germany

A review is presented on optical and scanning probe microscopic studies of liquid crystalline films. The free surface of ordinary liquids is smooth because the surface energy requires minimization of the surface area. Liquid crystals have some internal structure which may lead to a modulation of the surfaces. A suitable tool to study surface pattern is atomic force microscopy (AFM). It has a resolution in the order of nanometers but it can be used only on samples that are in a glassy state. Nematic surfaces of Schlieren textures show modulations caused by defects and inversion walls. The focal conic domains in homeotropic smectic textures show funnel shaped pits due to surfaces that tend to follow Dupin cyclides. Particularly rich and interesting surface patterns are shown by chiral mesophases. Cholesteric finger print textures show the defect lines that form near the surface in the transition layer between helix structure and unwound surface. Surfaces of blue phases reveal the lattice structure and allow to determine the lattice constant. The fan texture of chiral tilted smectic phase show a striped surface modulation caused by the helical twist.

In general the surface modulation turned out to be much stronger than expected on the basis of energy consideration. The cooling rate during sample preparation seems to be an important factor in pattern formation. It is presently investigated using a mesogenic side chain polymer.

#### A1.I02

THE FREE SURFACES OF CHOLESTERIC LIQUID CRYSTALS, R. Meister<sup>1</sup>, H. Dumoulin, M.-A. Hallé, and P. Pieranski, Université Paris Sud, Laboratoire de Physique des Solides, Bâtiment 510, F-91405 Orsay, France.

The free surfaces of mesogenic phases are not necessarily flat but can show reliefs. We have examined the free surfaces of oligomeric and polymeric cholesteric liquid crystals by means of Atomic Force Microscopy (AFM). The anchoring of the director at the free surface influences the equilibrium structure of the cholesteric phase near the free surface. For the case of a homeotropic anchoring, the topology of the problem requires the introduction of disclination lines. The minimization of the total free energy per unit surface area which takes account of the elastic distortion energy, the anchoring energy and of the surface tension leads to a smooth periodic surface relief and to an inclination of the "cholesteric planes" in the bulk with respect to the surface normal. The AFM images of microtome cuts of our materials support the proposed structures[1,2].

- [1] R. Meister, M.-A. Hallé, H. Dumoulin, and P. Pieranski, Phys. Rev. E, submitted.
- [2] R. Meister, H. Dumoulin, M.-A. Hallé, and P. Pieranski, J. Phys. II, submitted.

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A1.003

SURFACE INTERACTIONS IN PDLC STUDIED BY ELECTRIC FIELD SYNCHRONIZED NMR, P. Formoso, A. Golemme and G. Chidichimo, Dept. of Chemistry, University of Calabria, 87030 Rende (CS), Italy.

We have investigated the surface interactions between a nematic phase and different polymer surfaces in PDLC. We obtained information on the director distribution within droplets of different sizes from <sup>2</sup>H-NMR spectra from deuterated probe molecules dissolved in the dispersed mesophase. NMR acquisition has been synchronized with the turning on or off of an AC electric field of variable intensity normal to the static magnetic field. Since the typical NMR acquisition time is in this case around 1-2 ms, it was possible to follow the slower reorientation processes which are often found in PDLCs. Data were interpreted using a simple model describing the reorientation of the nematic under the influence of elastic, surface, field and viscous torques. This allowed, among other things, an estimation of the surface viscosity for the nematic phase E7 on different polymeric surfaces.

A1.O04

COMPARISON OF EXPERIMENTAL AND PHASE FIELD MODEL RESULTS ON THE GROWTH OF NEMATIC-SMECTIC-B INTERFACES.

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The study of the quasi-equilibrium and fast growing morphologies of a nematic-smectic-B interface in three components of a homologous series is presented. Experimental results are compared with those obtained from numerical simulations by means of a phase field model. Different shapes have been observed, from faceted in quasi-equilibrium to dendritic in rapid growth regime. The most important ingredients which determine these morphologies are surface tension anisotropy and undercooling, although kinetic effects have also to be taken into consideration, especially in the case of large undercooling and relatively small surface tension anisotropy. Qualitatively good agreement was found between the experiments and phase field model simulations.

A1.005

OBSERVATION OF CRITICAL FORCES IN A LIQUID CRYSTAL BY AN ATOMIC FORCE MICROSCOPE, <u>I.Muševič</u>, G.Slak and R.Blinc, J.Stefan Institute, Jamova 39, 61 000 Ljubljana, Slovenia

We report what we believe to be the first observation of critical phenomena in condensed matter using an Atomic Force Microscope. Using a temperature controlled AFM we have measured forces between two objects, immersed in an 8CB liquid crystal near the I-N phase transition. Deep in the isotropic phase we observe no force when the two surfaces are approaching, and a small attractive force of 0.1nN, when the two surfaces are moving apart. The phenomena are similar to the capillary force, and are interpreted as the local wetting of the sensing probe by the nearly-ordered liquid. Very near the phase transition into the nematic phase we observe a strong, nearly critical increase of this capillary force and the onset of a new phenomenon: a very weak but measurable attractive force of the order of 0.01nN, when the two surfaces are approaching. We conjecture that this is the so-called Casimir force [1], which is expected to arise in the vicinity of a critical point due to fluctuations of a massless director field [2,3].

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- [2] Th.W.Burkhardt, E.Eisenriegler, Phys. Rev.Lett. 74, 3189(1995).
- [3] A.Poniewierski and T.J.Sluckin, Liquid Crystals 2, 281(1987).



#### A1.006

TIME EVOLUTION OF THE STRUCTURE OF CONFINED SMECTIC-C\* FILMS<sup>†</sup>, Luz J. Martinez-Miranda<sup>1,2</sup>, Yushan Shi and Satyendra Kumar<sup>2</sup>, <sup>1</sup>Dept. of Materials and Nuclear Eng., Univ. of MD, College Park, MD, 20742, USA, <sup>2</sup> Dept. of Physics and Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA.

We have studied the structural evolution of films of the liquid crystal mixture mx5112, which has a room temperature sm-C\* phase, and a sm-C\* to sm-A transition at 46°C. The films are confined between two competing substrates, consisting of a 10 micrometer grating on glass and air. We have studied both the in-plane as well as the out-of-plane structure of the films. At room temperature the films exhibit a time-dependent oscillation between a sm-C\*-like and a sm-A-like structure, which depends on the history and thickness of the films, and which is aperiodic in nature. The in-plane signal exhibits a time dependent annealing effect along the direction of the gratings, and a more sm-A nature than the out-of-plane signal. We compare the time evolution of both signals and, finally discuss the temperature dependence of the oscillations.

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A1.I07

MESOGENIC BEHAVIORS OF 4-CARBOXY- AND 4-PROPENOXY-BENZO-15-CROWN-5 STILBAZOLYL ESTERS, J.J. Tsaih and <u>L.J. Yu</u>, Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137, Republic of China

Mesogens without terminal chain were obtained by connecting benzo-15-crown-5 and stilbazole with carboxy and propenoic acids. A nematic phase was observed for the later on cooling from 145 to 129°C. Hydrogen bond induced nematic and smectic phases with wide temperature ranges were observed for mixtures containing paraand meta-alkyloxy-benzoic acids as proton donors.

#### A1.008

PRESENT AND FUTURE OF THE LIQUID CRYSTALS CHEMISTRY, <u>V.S.Bezborodov\*</u>, Institute of Applied Physics Problems, 220064, Minsk, Belarus; R.Dąbrowski, Military University of Technology, 01-489 Warsaw, Poland

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The analysis of different synthetic schemes and technological aspects of the nematic and smectic liquid-crystalline compounds preparation have been done. The results of the analysis have shown that the Grignard reaction, Diels-Alder condensation and Nenitzescu method are suitable for the preparation of the LC derivatives of phenylcyclohexane. These methods do not allow to easily synthesize the LC compounds containing more than two cyclic fragments, containing lateral substituents other than methyl group in cyclohexane, cyclohexene or benzene rings, or containing the CH<sub>2</sub>CH<sub>2</sub> bridge between the cyclic fragments. The LC derivatives of cyclohexylbiphenyl or the other analogous LC compounds are usually prepared with low yields, using a cross-coupling, Grignard or a Friedel-Crafts reactions. Taking into account that these LC compounds may be prepared from the corresponding cyclohex-2-enones, 1,3-cyclohexanediones we compare these synthetic ways and propose to discuss the possibility of their use for the production of the LC materials.

#### A1.009

LIQUID CRYSTALS CONTAINING BORON CLUSTERS: DESIGN, SYNTHESIS, AND PROPERTIES, P. Kaszynski, J. Laska, and M. K. Patel, Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN, 37235, USA.

Recently, we introduced boron *closo*-clusters as new building blocks for the preparation of mesogenic materials [1]. Unlike any other fragment previously used in synthesis of liquid crystals, *closo*-clusters are 3-D σ-aromatic systems with 4-fold and 5-fold rotational axes. The electronic and geometrical properties of the clusters are unusual for mesogenic compounds and open possibilities for designing new structures and engineering molecular and bulk properties.

Here, we report our experimental and theoretical studies of the steric and electronic interaction of the *closo*-clusters with  $\sigma$  and  $\pi$  substituents. We also discuss the influence of these interactions and the shape of the conformational space that they define on the electronic and mesogenic properties of new materials.

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#### A1.010

HETEROCYCLIC ESTERS EXHIBITING FRUSTRATED LIQUID CRYSTAL PHASES, Alexander J. Seed, Michael Hird, and Peter Styring, School of Chemistry, University of Hull, Hull

A series of heterocyclic esters (structure 1) and the parent phenyl compound have been synthesised.

1 
$$C_{12}H_{25}O$$
  $X = 0$ , S and Se

The synthetic pathways to the compounds are outlined and include cross-coupling and metallation reactions. The mesomorphic behaviour of the compounds is discussed in relation to the change in molecular structure. The selenophene derivative exhibits some unusual novel frustrated phases in addition to the expected  $S_{C^*ferro}$ ,  $S_{C^*ferri}$  and  $S_{C^*anti}$  phases. The electrooptic properties of the compounds have been determined and are discussed.

A1.011

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LIQUID CRYSTALLINE CARBOHYDRATES FORMING SMECTIC, COLUMNAR AND CUBIC MESOPHASES, K. Borisch, S. Diele<sup>+</sup>, P. Göring<sup>+</sup> and C. Tschierske<sup>\*</sup>, Department of Organic and <sup>+</sup>Department of Physical Chemistry, University Halle, D-06099 Halle, Germany.

We have synthesized and investigated novel amphiphilic carbohydrate derivatives carrying one, two or three aliphatic chains. Depending on the number and the length of the alkyl chains smectic, bicontinous cubic, hexagonal columnar or inverted micellar thermotropic cubic mesophases were detected. By mixing a smectic single chain carbohydrate and a micellar cubic triple chain compound a hexagonal columnar phase can be induced. Similarly a hexagonal columnar phase was induced in the contact region between a bicontinuous and a micellar cubic mesophase. Using these mixing experiments we are now able - for the first time - to distinguish between the different structural types of cubic mesophases. This method can also be applied for the determination of the

structural types of thermotropic cubic mesophases of other amphiphilic compounds. Furthermore the mesophase type of these amphiphilic carbohydrates can be influenced by addition of protic solvents. For example the inverted micellar cubic mesophase of the three chain carbohydrates turns into a hexagonal columnar one on addition of ethylene glycol. Thus these materials can bridge the gap between thermotropic and lyotropic mesomorphism.

\*Supported by the Deutsche Forschungsgemeinschaft.

#### A2.I01

RECENT PROGRESS ON PHASE BOUNDARIES OF SOFT MATTER, J. B. Fournier, Materials Department, University of California, Santa Barbara, CA 93106, USA.

A general equation describing the equilibrium of soft matter's phase boundaries [1] is presented. It generalizes the Gibbs-Thomson equation, showing that the local phase transition temperature is shifted proportionally to the curvatures of the order parameter field at the interface, in addition to the usual shift proportional to the curvature of the interface. This equation is then used: (i) to explain the undulation instability of static smectic-C/isotropic interfaces [2]; (ii) to explain the shapes of cusped Langmuir monolayer domains. Soft matter domains exhibit 'quasicusps' instead of crystalline-like cusps, and boundary 'dips' that are forbidden in crystals [3].

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#### A2.102

THEORY OF CHIRAL INSTABILITIES IN SMECTIC-A LIQUID CRYSTALS, J. V. Selinger, B. R. Ratna, and R. Shashidhar, Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Code 6900, Washington, DC 20375, USA.

Chiral liquid crystals often exhibit instabilities in which the molecular director forms a periodic modulated pattern. In particular, thin films of the smectic-C\* phase undergo transitions from a state of uniform molecular tilt to a chiral striped texture. Here, we investigate whether similar chiral instabilities can occur in the smectic-A phase under an applied electric field. Using a continuum elastic theory, we determine whether the induced molecular tilt is uniform or whether it is modulated in a chiral striped texture. This theory shows that the uniform state becomes unstable when the system approaches the smectic-A—smectic-C\* transition, or when a high electric field is applied. Beyond that instability point, the system develops a chiral striped modulation in the molecular tilt, which induces a corresponding modulation in the smectic layers. We compare these predictions with observed striped textures in smectic-A liquid crystals.

A2.O03

COMPUTER SIMULATIONS OF POLAR GAY-BERNE SYSTEMS R. Berardi, S. Orlandi and C. Zannoni, Dip. di Chimica Fisica ed Inorganica dell'Università, 40136 Bologna, Italy

We show that the overall molecular dipole organization in a smectic liquid crystal formed of dipolar particles can be strongly influenced by the position of the dipole in the molecule. We study by large scale Monte Carlo simulations systems of attractive-repulsive "Gay-Berne" elongated ellipsoids [1,2] with an axial dipole at the center or near the end of the molecule and we show that monolayer smectic liquid crystals and modulated antiferroelectric bilayer domains like in the experimentally observed "antiphase"  $(S_{\tilde{A}})$  structures [3] are obtained in the two cases.

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A2.O04

## COMPUTER SIMULATION OF CHIRAL LIQUID CRYSTAL PHASES - A PHASE DIAGRAM OF THE CHIRAL GAY-BERNE DISCOGEN -

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Recently we performed simulations of chiral phases studying the chiral Gay-Berne fluid of calamitic molecules defined by adding a chiral potential to the Gay-Berne potential [1] and of chiral atropisomers given by joining two achiral Gay-Berne particles through a bond [2]. Here we present results of Monte-Carlo-studies for chiral discotic molecules which can serve as model systems for triphenylene compounds whose interesting properties are connected with intracolumnar and intercolumnar helical structures. The thermodynamic properties, the pitch of the chiral phases, order parameters, and correlation functions have been calculated in the chirality-temperature plane of the phase diagram. In order to study especially the equilibrium pitch in dependence on temperature and the chirality parameter self-determined boundary conditions have been applied.

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A2.O05

#### **DEMIXING OF BINARY LIQUID CRYSTALS: A SIMULATION STUDY**

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We have studied the mixing/demixing processes in liquid crystals on the molecular level. The Gay-Berne potential [1] and both simulation methods, Molecular Dynamics and Monte Carlo [2,3], were used. The structures were studied using various correlation functions, the order parameter and thermodynamic quantities. Two mixtures were in the center of our investigations: mixtures of molecules of lengths 3.0/1.5 and 3.0/6.0. The length 3.0 molecule is a standard model in computer simulations with the Gay-Berne potential and is well researched [4], while molecules of 1.5 are almost isotropic; on the other hand 6.0 is an extreme elongation. Some very interesting configurations were observed for different temperatures at compression and decompression.

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#### A2.006

COMPUTER-AIDED DESIGN OF FERROELECTRIC LIQUID CRYSTALS\*, Matthew A. Glaser and Noel A. Clark, Dept. of Physics, U. of Colorado, Boulder, CO, 80309, USA; Edgardo Garcia, Dept. of Chemistry, U. of Brazilia, Brazil; David M. Walba, Dept. of Chemistry and Biochemistry, U. of Colorado, Boulder, CO, 80309, USA.

Mean-field theory has become a well-established tool for interpreting experimental measurements on liquid crystals (LCs), most notably in the modeling of nematic-phase NMR spectra. Building on past experience with such mean-field models, we have recently begun to develop semi-empirical methods for the prediction of macroscopic properties of ferroelectric LCs (FLCs). Our approach combines a simple modular mean-field theory formalism with accurate molecular models derived from ab initio electronic structure calculations. Empirical input in the form of FTIR and NMR measurements on existing FLC materials is used to develop a "universal" mean-field parametrization for FLCs, which can in turn be used for the pre-synthesis prediction of FLC properties, including the spontaneous polarization density  $P_S$  and linear and nonlinear optical properties. This approach yields semi-quantitative agreement with experimental measurements of  $P_S$ . Applications to other FLC properties (e.g. second-order nonlinear optical susceptibility) will be discussed.

<sup>\*</sup>Work supported by NSF Materials Research Group Grant DMR 92-24168.

A2.I07

POLYMER-DISPERSED AND POLYMER-STABILIZED LIQUID CRYSTALS: RECENT RESULTS ON ANTIFERROELECTRIC AND CHIRAL DISCOTIC SYSTEMS H.-S. Kitzerow, J. Strauss and H. Bock\*, Iwan-N.-Stranski-Institute, Technical University Berlin, Sekr. ER 11, Str. des 17. Juni 135, 10623 Berlin, Germany.

During the last few years, polymer-dispersed and polymer-stabilized ferroelectric liquid crystals have been extensively studied [1-3]. Here, we present some studies on polymer composites containing either an antiferroelectric or a discotic ferroelectric liquid crystal. We have found that the presence of a polymer network changes the electrooptic switching behavior of an antiferroelectric liquid crystal so that it becomes possible to achieve grey scales in an antiferroelectric LCD. In addition, we report the first results about electrooptic effects in a polymer-dispersed discotic ferroelectric liquid crystal. In particular, we have found a thermo-electrooptic storage effect in the latter system.

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- \*Present address: Sharp, Edmund Halley Road, Science Park, Oxford OX4 4GA, England.

#### A2.008

MONODISPERSE OLIGIMERIC LIQUID CRYSTAL SUPERMOLECULES WITH DEFINED

#### **TOPOLOGY**

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Liquid-crystalline oligomeric materials are of interest because they are good candidates as systems which combine the properties of low molar mass materials eg low viscosity and fast switching times with the mechanical stability and the absence of crystallisation observed in some polymers. By using siloxane cores of cubic symmetry eg octakis-(hydrodimethylsiloxane)oktasilsesquioxane and tetrakis-(dimethylsiloxy)silane monodisperse oligomeric liquid crystalline supermolecules have been be synthesised. The use of cores of defined topology allows for the elimination of stereoisomers. For tetrahedral cores the attachment of side chains exhibiting tilted smectic phases favoured the formation of anticlinic phase behaviour. This was observed even in cases where such a phase behaviour could not be observed for the unreacted side chains. A typical feature of these materials are their comparatively low glass transition temperatures. The results obtained by optical and electro-optical studies, differential scanning calorimetry and X-ray diffraction are presented and compared with those for linear and cyclic analogues.

## A2.009

FERROELECTRIC PROPERTIES OF NOVEL CYCLIC SILOXANE OLIGOMERS, K. Grüneberg\*#, J. Naciri\*, D. Wolff°, R. Shashidhar\*, \*Naval Research Laboratory, Center for Bio/Molecular Science and Engineering, Code 6950, Washington, D.C., 20 375-5348, °Technical University of Berlin, Institute of Technical Chemistry, D-10623 Berlin, Germany

The design of ferroelectric cyclic siloxane oligomers is a new approach to overcome potential problems of low molar mass ferroelectric liquid crystals (FLC) (lack of mechanical stability) and device fabricating difficulties in FLC polymers due to increased viscosity. We investigated the influence of fluoro- and nitro-substitution in the mesogenic side group on the packing and structural features of cyclic siloxane oligomers by x-ray studies and computer simulation. We observe monolayer structures as well as strong tilde fluctuations in the smectic phases. The properties of one cyclic oligomer are compared to those of a linear siloxane polymer and it's unattached sidegroup consisting of the same mesogenic moiety as the cyclic siloxane oligomer. The ferroelectric and electroclinic response times as well as the tilt angles of the cyclic material are found to be similar to those of the monomer while the spontaneous polarization is comparable to that of the linear siloxane polymer.

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## A2.O10

SYNTHESIS AND PROPERTIES OF REGIOCONTROLLED CHIRAL LIQUID-CRYSTALLINE POLYESTERS, Feng Bai, L.-C. Chien\*, Rolfe Petschek, J. Ge³ and S.Z.D. Cheng³, Liquid Crystal Institute, Kent State University, Kent, OH 44242; Department of Physics, Case Western Reserve University; Department of Polymer Science, The University of Akron.

Synthesis and properties of a series of regiocontrolled chiral liquid-crystalline polyesters, 1, for nonlinear optics studies are presented.

$$NO_2 \stackrel{H}{=} CH_3$$
 $-CH_2 - CH_2 -$ 

For monomers the transition temperatures increase as the spacer length increases. The broad transition temperature ranges were resulted from the H-bonding interactions. The molecular archietechure of monomer allows one to preced the regiocontrolled polycondensations or melt processing. All the chiral polyesters exhibit the enantiomeric liquid-crystalline phases and good thermal stability.

This research was supported in part by the NSF ALCOM Center Grant DMR89-20147.

A2.011

OPTICAL STUDIES OF ANISOTROPIC NETWORKS IN POLYMER STABILIZED LIQUID CRYSTALS, Christine M. Hudson and L.C. Chien\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

Polymer stabilized liquid crystals form a class of unique materials in advanced flat panel display technology. We have studied the anisotropic polymer network formed upon photopolymerization of nematogenic azo containing diacrylates, 1, in a nematic solvent.

$$X = H, CH_3$$
  
 $Y = H, CF_3$ 

1

Mixtures of 1-5% of 1 in E-48 were filled into polyimide coated, parallel rubbed cells to enforce parallel surface anchoring. The polymer networks formed under these surface conditions were characterized by UV dichroism.

This research was supported in part by the NSF ALCOM Center Grant DMR89-20147.

A3.I01

WEAK CHIRALITY IN ORDERED DNA PHASES, Randall D. Kamien, Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, USA.

Recent experiments (R. Podgornik, et al) on aligned DNA show hexatic order with no sign of macroscopic chirality. I make the analogy between smectic liquid crystals and chiral hexatics and show how this chiral expulsion cannot be the result of a thermodynamic phase. In addition, I discuss the microscopic origin of chiral mesophases in liquid crystals. Within the context of central forces between "atoms" on "molecules", I show that chiral interactions can only occur if there are biaxial correlations between the mesogens, though possibly short-ranged, leading to small cholesteric pitches in helical molecules.

A3.I02

# Melting of Phospholipid Tubules

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The melting of lipid based microcylinders (tubules) has been investigated for systems with single and multiple bilayer walls using high field, magnetic birefringence and precision microcalorimetry. The pretransitional behavior of both the magnetic birefringence and the specific heat is very different in tubules with a single bilayer wall from that of tubules with multiple bilayers.

A3.003

MODEL PROPOSED FOR THE CUBIC PHASE IDENTIFIED IN A TERNARY LYOTROPIC SYSTEM, Y. Hendrikx, and B. Pansu, Laboratoire de Physique des Solides, Bât. 510, Université Paris-Sud, 91405 Orsay cedex, France.

A cubic phase has been identified in the ternary lyotropic sodium decyl sulfate / 2-octanol / water system. This cubic phase lies in between a cylindrical and a lamellar phase. Epitaxial relations between the different phases are pointed out. According to the Bragg reflexions, the cubic phase is a centred one and its structure reminds that of the cubic phase observed in the binary sodium dodecyl sulfate / water system. The proposed space group for the latter is Im3m (1). This cubic phase is made of two systems of interpenetrated rods of amphiphilic molecules embedded in a continuous water medium. However this model is not compatible with the physico-chemical parameters imposed by our investigated system and therefore we propose a new model for the cubic phase: the rods of both sub-lattices are no longer cylinders but ribbons and in that case the space group is Im3.

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A3.004

PHYSICOCHEMICAL CHARACTERIZATION OF LIQUID CRYSTALLINE PHASES IN MODEL BILE AND LIPID DIGESTIVE MIXTURES. P. W. Westerman\*†, R. Jacquet\*, B. Quinn\*, P. Rinaldi§ and Y. Sun§, \*Northeastern Ohio Universities College of Medicine, Rootstown, Ohio 44272; †Kent State University, Kent, Ohio 44242 and §University of Akron, Akron, Ohio 44325.

The phase properties of aqueous dispersions of model bile mixtures containing cholesterol, lecithin and bile salts, and model mixed lipid digestive mixtures containing cholesterol, fatty acids, monoglycerides, lecithin and bile salts, have been characterized by  $^2H$  NMR. We have chemically incorporated a deuteriomethyl (CD<sub>3</sub>) group into one lipid component, and utilized the differences in magnitude of the motionally-averaged quadrupole splitting ( $\delta\nu$ ) to determine by spectral integration, the distribution of that lipid between solid, multilamellar and micellar phases. By  $^2H$ -labelling both cholesterol and lecithin in a system of a given overall composition we have used the different CD<sub>3</sub> chemical shifts and  $\delta\nu$  values, to determine directly the chemical composition of the micellar and multilamellar phases. The mechanism by which bile salts disrupt lipid lamellae has been investigated by  $^2H$  and  $^{31}P$  NMR. Addition of detergent bile salts converts a lamellar phase into micelles via an intermediate phase of cylindrical symmetry. Models for this phase and the micelles have been proposed on the basis of 1D and 2D  $^1H$  NMR at 600 MHz as well as pulsed field gradient self-diffusion measurements.

A3.O05

DIRECTOR FLUCTUATIONS AND VISCOELASTIC PROPERTIES IN BIOMEMBRANES: THE EFFECT OF CHOLESTEROL AND PROTEINS, G. Althoff, N. Heaton, G. Gröber, S. Prosser, M. Vilfan\*, and G. Kothe, Dept. Physical Chemistry, University of Freiburg, Albertstr. 21, Germany, \*Josef Stefan Institute, University of Ljubljana, Jamova 39, Ljubljana, Slovenia.

The liquid crystalline nature of biomembranes is of fundamental importance in determining the biological function of these materials. The symmetry axis of the local orientational distribution serves to define a director at a particular point in the membrane. Collective motions of the constituent molecules are then reflected by fluctuations of the local director. Pulse frequency dependent transverse <sup>31</sup>P and <sup>2</sup>H spin relaxation techniques have been employed to characterize these thermal fluctuations [1]. Analysis of the dispersion profiles yields values for the splay elastic constant and the effective viscosity of various biomembranes, containing cholesterol and proteins [2]. Measurements at four different magnetic field strengths indicate that the low frequency plateau in the dispersion profile is due to magnetic damping of the collective modes.

E. Dufourc, C. Mayer, J. Stohrer, G. Althoff, and G. Kothe, Biophys. J. 61, 42 (1992).
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#### A3.006

MICELLAR CHANGES AT H-N<sub>c</sub> AND N<sub>c</sub>-N<sub>bx</sub>-N<sub>d</sub> PHASE TRANSITIONS IN LYOTROPIC LIQUID CRYSTALS, <u>L. Q. Amaral</u> and O. Santin Filho<sup>2</sup>, 1 - Institute of Physics, University of São Paulo, C.P.66318, 05389-970 - São Paulo, SP, Brasil; 2 - Universidade Estadual de Maringá, PR, Brasil.

Previous ideas [1] regarding changes of micellar form from ellipsoid to spherocylinder (SC) as a pre-requisite for the occurrence of the isotropic (I)-hexagonal (H) phase transition are extended to transitions to nematic (N) phases. Calculations of the elastic bending energy of the polar-apolar micellar interface as a function of the surfactant parameter  $p_o = v/at$  (v = hydrophobic chain volume, a = polar head area, t = chain length) show [2] that a change of form SC  $\rightarrow$  rectangular tablet (RT)  $\rightarrow$  square tablet (ST) is expected both for increasing additions of co-surfactant and changes of  $p_o$  values. A remarkable agreement is obtained with observed phase transitions for changes in concentration and temperature in the systems with SDS (sodium decyl sulfate), KL (potassium laurate) and SLS (sodium dodecyl sulfate) as surfactants and decanol as co-surfactant. The results here reported together with recent proposals [3] regarding the structure of phase H and its transitions to cubic phases lead to a novel insight on lyomesophases.

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Phys.Rev.E 50, 1678 (1994); P. Mariani et al, J.Physique II 4, 1393 (1994).

A3.I07

OPTICALLY INDUCED DIRECTOR ORIENTATION IN DYE DOPED LIQUID CRYSTALS, A. F. Klittnick, T. Bellini, N. A. Clark, Physics Department, University of Colorado, Boulder, CO, 80309, USA.

We illuminate aligned dye doped liquid crystals with the interference fringe pattern from crossed 514nm Ar laser beams. The optical intensity gradient, in the direction normal to the fringe planes, in conjuction with an applied DC field, induces in the liquid crystal a modulation of the director. The resulting refractive index modulation, which disappears when the director is parallel to the fringe plane, is probed by the diffraction of a HeNe laser. The dynamic behavior of this photorefractive effect and related effects with additional AC and DC fields applied will be presented and discussed.

Work supported by NSF Grant DMR 92-23729 and ARO Grant DAAG 04-939G-0164.

#### A3.008

AZIMUTHAL SURFACE ANCHORING ENERGY IN PHOTO-INDUCED PVCi OPTICAL ANISOTROPIC ALIGNMENT FILMS, Xiang Tong LI, Dong He PEI, Yasufumi IIMURA and Shunsuke KOBAYASHI, Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, JAPAN

Liquid crystal alignment effect in polyvinyl cinnamate (PVCi) films induced by the irradiation of linearly polarized ultraviolet (UV) light has been investigated. The present research was carried out by analyzing the azimuthal surface anchoring energy for nematic liquid crystal (5CB) as a function of birefringence and anisotropic UV absorption that are induced by the UV irradiation on PVCi films. The azimuthal surface anchoring energy was evaluated by measuring the width of Neel walls and the refractive indices, where  $n_o$  for the ordinary light and  $n_e$  for the extraordinary light were measured by the Abeles method. Meanwhile, the anisotropic UV absorption spectra were measured using a spectrometer. As a result, it is found that the azimuthal surface anchoring energy increases with the increase of birefringence and anisotropy in the UV spectra for the PVCi films, in consistent with the theory of Okano, Matsuura and Kobayashi  $^{10}$ .

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## A3.009

ORIENTATION AND SURFACE ANCHORING OF NEMATIC LIQUID CRYSTALS ON LINEARLY POLYMERIZED PHOTOPOLYMERS, H. G. Galabova, D. W. Allender\*, and J. Chen, Liquid Crystal Institute and Physics Department, Kent State University, Kent, Ohio, 44242, USA.

The liquid crystal orientation on a polymer-coated solid substrate exposed to linearly polarized UV light has been studied. The angular distribution of the polymer side chains was derived as a function of exposure time using a simple assumption about the probability for crosslinking of two side chains. The liquid crystal was assumed to be weakly anchored to the surface but have the same degree of order and orientation as those of the polymer side chains. The polar and the azimuthal anchoring strengths were estimated as a function of exposure time and the decay of the order away from the surface was calculated using the Landau-de Gennes theory.

\*Supported by NSF ALCOM Grant DMR 89-20147.

# A3.O10

# COMPETITION OF SELF-ORGANIZATION AND PHOTOORIENTATION IN LC POLYMERS

J. Stumpe, L. Läsker, Th. Fischer, M. Rutloh, R. Ruhmann, Dept. of Chem., Humboldt-Universität Berlin, Germany

On irradiation with linearly polarized light optical anisotropy is induced or reversibly modified in films of photochromic LC polymers due to photoorientation. This process in the steady state of the photoisomerization of azobenzenes effects a reorientation of the photochromic groups towards a direction perpendicular to the electric field vector of the incident light. Under certain circumstances the reorientation of these moieties may cause a cooperative reorientation of the non-photochromic side groups in the same direction. In this way an optical axis is generated in in the glassy state of initially isotropic films by a photochemically induced physical reorientation process. The resulting values of light-induced birefringence up to  $\Delta$  n 0,3 are close to those for aligned LCP films.

In aligned films of LCP's a competition takes place between the primary order and the ordering tendency of the linearly polarized light. In polymers with a high tendency of self-organization the reorientation process may be suppressed by the inital order. On the other hand, efficient orientational processes occur in polymers with a low enthalpic stability of the liquid crystalline phases and in amorphous polymers. Initally isotropic films of such polymers combine the easy preparation with the opportunity to induce LC-like optical properties. Moreover, the self-organization of LCP's on annealing cause a significant amplification of the photochemically induced optical anisotropy whereas the orientational order generated in the glassy state acts as an initializing force causing a macroscopic alignment.

A3.011

ANCHORING ENERGY AT THE INTERFACE BETWEEN OPTICALLY ALIGNED NEMATIC LC AND UV-EXPOSED POLYIMIDE, M. Hasegawa, IBM Research, Tokyo Research Laboratory, 1623-14, Shimotsuruma, Yamato, 242, JAPAN

The anchoring energy at the interface between nematic LC and linearly polarized UV-exposed polyimide was measured by using the method of applying a strong electric field [1]. We reported previously that linearly polarized UV-exposed polymer films showed a homogeneous alignment of nematic LC, and suggested a model for that alignment [2]. However, the alignment mechanism is not yet clear. To clarify this mechanism, we measured the azimuthal and polar anchoring energy and the IR absorption spectrums by varying the energy of the UV to which the polyimide films were exposed. We discuss a change in the chemical structure of polyimide during UV exposure, using the results of IR absorption spectrums. A UV alignment model is suggested on the basis of a relation between the change in the chemical structure of the polyimide and the anchoring energy of the interface.

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A3.O12

STABILIZATION OF POLYMER DISPERSED LIQUID CRYSTALS USING SURFACE ACTIVE AGENTS, C. Snively and J. L. Koenig\*, Macromolecular Science Department, Case western Reserve University, Cleveland, OH 44106, USA.

In this study, surface active agents were used in the preparation of polymer dispersed liquid crystals (PDLCs) by temperature induced phase separation. The surfactants Tween 20, a mixture of long chain carboxylic acids, and oleic acid were used to stabilize the liquid crystal 4-n-pentyl-4'-cyanobiphenyl (5CB) in a poly(iso-butyl methacrylate) matrix. The PDLCs formed using the surfactants exhibited more uniform particle sizes and greater particle size stability than comparable systems which contained no surfactant. The stabilized systems maintained their properties after being switched over 100,000 times. Also, the response to an applied electric field was shown to be faster for the stabilized PDLC systems.

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# Liquid Crystal Devices and Devices for Liquid Crystals

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With the wide spread use of liquid crystal devices, in applications ranging from simple calculators to fairly sophisticated Computer displays, it is hard to imagine what the world would look like if there were no liquid crystal materials. Progress in this field has been fairly rapid with clever use of this materials in a wide range of applications. The current primary focus in industry is for displays because of the potential market for these products however the focus of the talk will be on other applications of liquid crystals ranging from femtosecond pulse shaping to the use of these materials in complex telecommunication switches.

The wide range of available liquid crystal materials and the variety of structures they exhibit, allows devices structures to be made which are perhaps not possible by any other material. For example the nematic phase, having the most elementary liquid crystalline order, can be used in untwisted structure to produce devices for pulse shaping and beam steering, while the twisted structure can be used to produce optical intensity modulators with contrast ratio exceeding 105, which makes these devices extremely useful in communications applications where such performance is often necessary.

In developing these devices one often encounters unexpected behavior which often lead to new insight into the materials themselves. Some of these will be discussed in the talk. Such discoveries often leads to the realization that the process of construction of devices can lead to new avenues of research, and that the applied and fundamental sciences are closely coupled. This is well illustrated by our work in developing fairly simple liquid crystal Fabry-Perot structures for optical communications, which can also be used to gain understanding of how the discotic liquid crystals distort in presence of an electric field.

#### B1.I01

DIELECTRIC AND OPTICAL PROPERTIES IN PDLC FILMS, <sup>†</sup> T.J. Sluckin, V.Yu. Reshetnyak, C.J. Walden and S.J. Cox. Faculty of Mathematical Studies, University of Southampton, Southampton SQ17 1RJ, UK.

We review recent work in Southampton on a more comprehensive theory of PDLC film properties. Dielectric properties of PDLC films are modelled using effective medium theories of the Maxwell-Garnett family. PDLC films present a number of non-standard features including field dependent and anisotropic response. We present a self-consistent theory which allows for both hipolar and radial droplets. Field-induced recrientation of bipolar droplet easy axes plays an important role in dielectric and thus optical phenomena. We present results for light scattering by liquid crystal droplets using modified Mic theory in an effective medium, and compare the results to standard ADA and Rayleigh-Gans theories.

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 Work supported by (UK) EPSRC Grants GR/J88111. GR/K36281.

#### B1.I02

# SOME EFFECTS OF ANCHORING ON DROPLET STRUCTURE AND DEVICE PROPERTIES IN POLYMER-DISPERSED LIQUID CRYSTAL MATERIALS

Paul S. Drzaic, Raychem Corporation, Menlo Park, CA 94205 USA

Reduction of the orientation field is an important goal in many areas of polymer dispersed liquid crystal development. We have found that the addition of certain carboxylic acids to polyvinylalcohol-based PDLC film produces lowered operating voltages through reduction of the anchoring interaction of the LC/polymer interface. Selection of the alkyl chain length and acid concentration can be used to select either strong or weak polar anchoring in either parallel or perpendicular alignment. The type of anchoring, in turn, affects both the droplet structure and various electro-optical properties of the PDLC device. Along with examples of these effects, a brief description of current PDLC applications will also be provided.

B1.003

COLOR PIXELIZATION OF REFLECTIVE CHOLESTERIC DISPLAYS, <u>L.-C. Chien</u>\*, U. Müller, Fred Vicéntini, and Yuhui Lin, Liquid Crystal Institute, Chemical Physics and NSF ALCOM Center, Kent State University, Kent, OH 44242.

We present the method of adjusting the pitch of a cholesteric material, utilizing a tunable chiral material (TCM) in conjunction with photolithography, for color pixelization of reflective cholesteric displays (RCDs). The Bragg reflective colors are photo-tuned by adjusting the chirality of each pixel. An example of using a binaphthol derivative as the TCM for color patterning and its chirality decreases as the UV dose increase will be discussed. A monomeric binaphthol is synthesized for inclusion in a cholesteric liquid crystal and a diacrylate monomer. Subsequent photopolymerizing the monomers resulted in the incorporation of TCM molecules onto the polymer network. Additional UV radiation allows one to pattern the color. The method of forming polymer walls to prevent the color diffusion between different color regions will also be presented.

This research was supported in part by the ARPA Low Power Displays Contract # N61331-94-K-0042.

**B1.O04** 

MECHANISMS OF ORIENTATIONAL ORDERING OF BIPOLAR NEMATIC DROPS IN A STRETCHED PVA MATRIX, O. A. Aphonin, Department of Physics, University of Saratov, Astrakhanskaya 83, Saratov 410071, Russia.

The orientational ordering of nematic (5CB) drops with the bipolar director-field configuration, embedded in a uniaxially stretched polyvinyl alcohol matrix, is studied by polarizing optical microscopy. It is found that at small matrix deformations each bipolar structure is captured by the surface of the drop cavity but, if the drop non-sphericity further increases, there comes a point where the drop abruptly reorients parallel to the long cavity axis. The heating of the slightly elongated polymer matrix above its glass transition temperature is found to eliminate the captured structures and produces the irreversible uniaxial orientation of the sample. The obtained information is analyzed in terms of three models taking into account the microrelief of the drop surface, the ordered organization of polymer molecules at the drop boundary, and the initial non-sphericity of drop cavity, respectively. It is inferred that the formation of the supramolecular polymer structure at the matrix/drop interface during the matrix curing process and its changes with stretching and heating are the governing factors responsible for the observed phenomena.

B1.005

INFRARED AND NEUTRON SPECTROSCOPY OF LIQUID CRYSTAL COMPOSITES, L. Bata, K. Fodor-Csorba, S. Holly\*, A. Jákli, Gy. Káli, T. Paksi, L. Rosta and A. Vajda, Research Institute for Solid State Physics, H-1525 Budapest, P. O. Box, 49, Hungary, \*Central Research Institute for Chemistry, H-1525 Budapest, P.O.Box 49, Hungary

The structure of polymers and of 7nm pyrogenic silica particles dispersed in low concentration (1-3wt%) in nematic, cholesteric and smectic liquid crystals were studied by infrared and neutron spectroscopy. IR spectroscopy gave us information about the polymerisation process. It was found that in addition of the branched polymers large amount of olygomers are also present. Neutron spectroscopy revealed the structure of the dispersed particles. In the polymer composites first the larger, then the smaller polymer units separate out on cooling yielding rough fibres with average diameters in the range of a few hundred Angstroms. The glass spheres form clusters typically of 200 Angstrom sizes. Both the polymer fibres and silica clusters are plastic and can adopt the alignment of the liquid crystal matrix. In turn their structure mainly remains after thermal treatments and restore the previous director alignment of the liquid crystal if it is lost by heating to the isotropic phase. The interaction between the dispersed units and the liquid crystal molecules will be discussed and be compared for the different systems.

#### **B1.006**

MODELLING STRUCTURE FORMATION IN POLYMER-DISPERSED LIQUID CRYSTALS, P. I. C. Teixeira and <u>B. M. Mulder</u>, FOM Institute for Atomic and Molecular Physics, Kruislaan 407, NL-1098 SJ Amsterdam, The Netherlands

We present models for the dynamics of formation and morphology of polymer-dispersed liquid crystals (PDLCs). These incorporate the key physical ingredients of the actual fabrication processes: polymerisation/gelation, phase separation, and growth and stabilisation of a spatially inhomogenous structure. We model phase separation of the initial pre-PDLC mixture by the cell dynamical systems (CDS) method of Oono and Puri [1]. The polymer gel/matrix is described by a phase field which also obeys a CDS equation. Growth is assumed to occur at the gel/matrix surface. Finally, structure stabilisation is achieved by inclusion of a non-local term which mimics gel cohesion. We have performed numerical calculations on a two-dimensional system for a composition of 30% LC + 70% monomer or polymer. Depending on the the polymerisation method modelled we get either a fairly monodisperse dispersion of LC droplets (PIPS) [2] or, a quench rate dependent, broad droplet size distribution (TIPS). Results obtained from either model are consistent with observations on real PDLCs.

- [1] Y. Oono and S. Puri Phys. Rev. Lett. 58 836 (1987)
- [2] P. I. C. Teixeira and B. M. Mulder Phys. Rev. E 53 1803 (1996)

**B2.I01** 

# PECULIAR MACROMOLECULAR ORGANIZATION IN NEMATIC POLY(URETHANE-ESTER)S Oriano Francescangeli

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The results of a structural analysis by X-ray diffraction of a series of thermotropic poly(urethane-ester)s TDI-CmCn, prepared from various mesogenic alkylene di[4-(ω-hydroxyalkyloxy-4-oxybenzoyl)oxybenzoate]s (CmCn; m=2, 4 or 6, and n=4, 6, 8 or 10) and 2,4-toluenediisocyanate (TDI) [1], are reported. Evidence is provided for the formation of two different nematic mesophases in the polymers [2]. Whereas samples TDI-C2C6, TDI-C6C4, and TDI-C6C10 form one nematic mesophase, samples TDI-C4C6, TDI-C6C6, and TDI-C6C8 exhibit both cybotactic nematic (N2) and conventional nematic (N1) mesophases in a sequence with increasing temperature, which are connected by a firstorder transition at T<sub>N2-N1</sub>. Indeed, these polymers offer the first example of a class of even-spaced main-chain polymers exhibiting different nematic phases in a sequence. The ability to form intermolecular hydrogen bonding was found to play a role in enhancing the lateral packing strength between adjacent chains thus stabilizing the cybotactic nematic mesophase. In fact, the transition to the conventional nematic mesophase is accompained by a breaking of the hydrogen bonding structure. In addition, the highly organized cybotactic nematic structure results in a peculiar dynamic mechanical behavior. The analysis of the X-ray diffraction patterns suggests that two structural arrangements, namely smectic C-like and conventional nematic structures, coexist inside the cybotactic nematic mesophases. The cybotactic clusters present an asymmetrical ellipsoidal-like shape: the average dimension of the cybotactic clusters along the director is comprised between ~ 260 Å and ~ 560 Å whereas the average dimension perpendicular to the director ranges from ~ 130 Å to ~ 270 Å. The longitudinal coherence length increases regularly as the length of the flexible spacer increases whereas the transversal coherence length reaches a constant value thus indicating that the flexible spacer plays a fundamental role in the ordering process. On the other hand, the correlation length within the nematic surrounding is comprised between 38 and 45 Å, which is of the order of the molecular length. These findings highlight the multidomain nature of the cybotactic nematic mesophase [3].

[1] E. Chiellini et al., Mol. Cryst. Liq. Cryst., 243, 135 (1994); [2] O. Francescangeli et al., Jour. Polym. Sci. Polym. Phys., 33, 699 (1995); [3] O. Francescangeli et al., Phys. Rev. E, submitted.

**B2.I02** 

# **BOWL-SHAPED LCS AT THE AIR-WATER INTERFACE**

Abdel-Illah EL ABED

GRPB, Universite Rene Descartes, 45 rue des Saints-Peres 75006 Paris, France

We studied, at the air-water interface, monolayers of bowl-shaped liquid crystals (BLC's). These compounds exhibit columnar mesophases. They consist of an either rigid or flexible central core to which are attached several hydrophobic aliphatic chains. We investigate experimentally in this work, using different techniques: Surface pressure and displacement current versus molecular area isotherms, optical and Brewster angle microscopy, molecular organization of these compounds at the air-water interface and discuss some of their structural aspects. We show also the flexibility of the central core and its effect on the structure of the monomolecular films. We studied also, their molecular transfer process from 2D to 3D phases.

#### B2.O03

#### WEDGE-SHAPED MOLECULES WITH RIGID PERFLUORINATED CHAINS, E. Dietzmann,

W. Weissflog, D. Lose\*, S. Diele\*, Max-Planck-Research Group Liquid Crystalline Systems, Muehlpforte 1, 06108 Halle, Germany, \*Martin-Luther-University Halle-Wittenberg, Institute of Physical Chemistry, Muehlpforte 1, 06108 Halle, Germany

We synthesized new laterally aryl and terminally branched (so-called swallow-tailed compounds) molecules containing rigid perfluorinated chains. They can be characterized as wedge-shaped molecules consisting of chemically and sterically incompatible molecular segments. They arrange antiparallel to each other to reach a higher packing density. Such compounds have higher clearing temperatures and smectic A and smectic C phases in a broader temperature range compared to the nonfluorinated reference substances. The position of the fluorination is of interest especially in the case of the terminal branched molecules. But the main question of our investigations was: How do these molecules arrange in pure compounds and in mixtures of two different molecules with opposite direction of the dipoles? That's why we carried out mixing investigations and X-ray measurements. The strong competition between the steric, dipolar and immiscibility forces has led to the occurrence of some very interesting phase sequences. We found in dependence on the length of the perfluorinated chains in the swallow-tailed compounds with the fluorination in the nonbranched end undulated structures or besides the smectic phases rectangular columnar phases. This is the first case of simple swallow-tailed molecules having a columnar and lamellar phases together in one compound.

#### **B2.O04**

CHOLESTERIC CARBOHYDRATE LIQUID CRYSTALS INCORPORATING AN INTACT GLUCOPYRANOSE MOIETY E. Smits, J.B.F.N. Engberts and R.M. Kellogg, University of Groningen, Nijenborgh 4, 9747 AG Groningen, H.A. van Doren, Netherlands Institute for Carbohydrate Research, Rouaanstraat 27, 9723 CC Groningen, the Netherlands.

The mesophase of <u>amphiphilic</u> monosaccharide liquid crystals is determined by their overall molecular shape; the amphiphilic character most likely impedes the formation of chiral mesophases. Recently, we have shown that the following rigid moiety I can serve as the structural basis for 'non-amphiphilic' carbohydrate mesogens. One can obtain smectogens when R is

HO OH X R'

carbohydrate mesogens.<sup>2</sup> One can obtain smectogens when R is an aromatic Schiff base. When R is a benzoate ester, several derivatives of I display a cholesteric phase. The latter are the first monosaccharide derivatives containing a fully intact glucopyranose ring and two vicinal OH-groups with a thermotropic chiral mesophase. We are currently investigating the influence of the orientation of the dipole moment of the aromatic moiety and the type of linkage between the mesogenic and carbohydrate moieties on the liquid-crystalline behavior of the derivatives.

1. H.A. van Doren and K.R. Terpstra, J. Mater. Chem., 1995, 12, 2153.

2. E. Smits, J.B.F.N. Engberts, R.M. Kellogg and H.A. van Doren, Mol. Cryst. Liq. Cryst. 1995, 260, 185.

#### **B2.O05**

NOVEL GLASS-FORMING LIQUID CRYSTALS: MOLECULAR DESIGN AND SYNTHESIS\*, S. H. Chen\*\*, H. Shi, and J.C. Mastrangelo, Center for Optoelectronics and Imaging, University of Rochester, 240 E. River Rd., Rochester, New York 14623-1212.

Liquid crystals (LCs) are making major inroads in various optical and optoelectronic technologies. In applications that do not involve field-induced molecular reorientation, it is desirable that mesomorphic order be frozen in a glassy matrix to provide long-term stability and environmental durability. To achieve this goal, a molecular design approach has been pursued in which a subtle balance between vitrification (i.e., disorder) and LC mesomorphism (i.e., orientational order) is struck by having the mesogenic group attached to a volume-excluding core via a flexible spacer with a well-defined overall stereochemistry. In addition, chiral and various functional moieties can be incorporated to form a diversity of multifunctional materials. This molecular design approach will be illustrated with nematic and chiral-nematic LCs using high optical birefringence nematogens and chiral moieties with cyclohexane, bicyclooctene, adamantane, and cubane as volume-excluding central cores. The factors contributing to morphological stability will be identified, and potential applications to the fabrication of optical filters and waveplates will be demonstrated. \*Supported by MITI (Japan), NSF Grant CTS-9500737, Kaiser Electronics, and DOE Grant DE-FC03-92SF19460.

**B2.O06** 

STRUCTURAL INVESTIGATION OF SMECTIC Q PHASE, D. Bennemann, G. Heppke, D. Lötzsch, Iwan-N-Stranski-Institut, Technishe Universität Berlin, Sekr.11, Strasse des 17 Juni 135, 10623 Berlin, Germany, and A.-M. Levelut, Laboratoire de Physique des Solides, Université Paris-Sud, F91405 Orsay cedex, France.

Some mesogenic chiral compounds show a smectic Q phase just below the clearing point [1]. The molecules are in a liquid state but they are organized on a tridimensional tetragonal lattice. At lower temperature the only possible mesophase - mesophase transformation is toward an antiferroelectric smectic. Three different tetragonal lattices have been identified. These phases can be considered as crystalline arrays of twist grain boundaries (which can form a triply periodic minimal surface) inside an antiferroelectric smectic. The twist grain boundaries perpendicular to the smectic planes divide the smectic structure in narrow sheets (their width compare to the molecular length), the smectic planes are twisted by an angle of  $\pi/2$  on each side of a boundary and the successive sheets correspond one each other by a  $4_1$  or a  $4_2$  helical axis.

[1] D. Bennemann, G. Heppke, A.-M. Levelut and D. Lötzsch, Molecular Crystals Liquid Crystals, 260, 351 (1995)

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**B3.I01** 

MOLECULAR REORIENTATIONS AND RELAXTION IN PHOTOSENSITIVE LCP'S: IN-DUCED BIREFRINGENCE AND POLARIZED MICRO-RAMAN SPECTROSCOPY, M. P. Fontana, C. Paris, M. Polli, Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, University of Parma, 1-43100 Parma, Italy.

The side chain LCP azopolyacrylate has interesting photoisomerization effects upon absorption of light by the azo-group in the side chain [1]. The material also easily forms a glassy structure, with  $T_g = 20$ °C. In this work we show that upon illumination with polarized blue laser light the molecules reorient perpendicularly to the polarization direction of the incident light. We demonstrate this on the microscopic scale by polarized micro-Raman spectroscopy of the illuminated zone. The reorientation process was followed in time as a function of incident light power and at different temperatures in the neighborhood of  $T_g$ , by monitoring the induced birefringence. Thus we were able to determine molecular relaxation times and their behavior in the neighborhood of the glass transition in this fragile glass, using light to take the system out of equilibrium.

[1] S. Angeloni et al., Liquid Crystals 4, 513 (1989).

**B3.I02** 

FERROELECTRIC LIQUID CRYSTALS FOR SECOND ORDER NONLINEAR OPTICS, <u>David M. Walba</u>,\* Daniel J. Dyer,\* Xin Hua Chen,\* Joel A. Drewes,\* Noel A. Clark,<sup>†</sup> and Renfan Shao,<sup>†</sup> \*Department of Chemistry and Biochemistry, <sup>†</sup>Department of Physics, and Optoelectronic Computing Systems Center, University of Colorado, Boulder, Colorado 80309

Smectic C\* ferroelectric liquid crystals (C\*FLCs) are potentially attractive as materials for second order nonlinear optics (NLO) applications. But, to realize this potential substantial increase in  $\chi^{(2)}$  must be achieved. This seems problematical since organic structures with large  $\beta$  typically possess two rings with a conjugating spacer, which should be oriented along the polar axis in a bulk sample to achieve large  $\chi^{(2)}$ . However, such structures typically orient parallel to the director in LCs, while in C\*FLCs the polar axis is normal to the director. We present here recent results describing a solution to this problem: "Sideways dimer" mesogenic structures [1] providing orientation of functional arrays with large  $\beta$ , such as those found in the NLO dyes Disperse Red 1 and Dimethylaminonitrectilpene, normal to the director in chiral smectic LCs. This system has provided several excellent A\* and C\* mesogens, and the first examples of smectic phases with negative birefringence.

[1] D. M. Walba, D. J. Dyer, T. Sierra, P. L. Cobben, R. Shao and N. A. Clark, J. Am. Chem. Soc., 118, 1211-1212 (1996).

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**B3.003** 

LIGHT-INDUCED MOLECULAR REORIENTATION AND CHANGE OF INDUCED POLARIZATION IN THE CHIRAL SMECTIC A PHASE, <u>D. Hermann</u>, L. Komitov, F. Simoni<sup>n</sup>, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden, <sup>n</sup>Dipartimento di Scienze dei Materiali e della Terra e Istituto Nazionale per la Fisica della Materia, Università di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy.

Recently, we studied non-linear optical effects in the Sm A\* phase, excited by a continuous-wave laser beam from an Ar\*-ion laser at 514.5 nm, monitoring the reorientation of the director (optic axis), upon laser irradiation, by means of a pump-probe technique. The present work is a continuation of these studies. We have examined samples with two room temperature SmA\* mixtures exhibiting a large electroclinic effect. Some of the samples were doped with the dye D-2. We found that the rotation of the optic axis is a local effect, i.e. the orientation of the director changes transversally across the pump laser beam. Moreover, the local director orientation changes slightly in time, and seems to be opposite on opposite sides of the center of the pump laser beam. Finally, apart from a more efficient heating of the sample, we have observed a permanent texture change in the dye-doped samples in terms of a smectic layer rotation. This effect took place when the sample is irradiated by the pump laser beam while applying an electric ac-field and was not found in the undoped samples.

**B3.004** 

PHOTOINDUCED ANISOTROPY IN DYE-DOPED POLYMER ALIGNMENT LAYERS, T. Kosa, P. Palffy-Muhoray, Liquid Crystal Institute, Kent State University, Kent, OH 44242 USA

We study the anisotropy induced by polarized light in dye-doped alignment layers. We measure the photoinduced birefringence as well as the anchoring strength of some azo-dyes in polyimide as a function of intensity, exposure time, and concentration. We propose a simple model for the orientation of the dye under the influence of the light field and the resulting anchoring potential.

**B3.O05** 

ANOMALOUS OPTICAL KERR EFFECT IN DYE-DOPED LIQUID CRYSTALS IN THE ISOTROPIC PHASE

D. Paparo, L. Marruci, G. Abbate, E. Santamato, P. Lehnert\*, M. Kreuzer\*, and T. Vogeler\*, INFM and Dipartimento di Scienze Fisiche, PAD 20, Mostra D'Oltremare, 80125 Napoli, Italy, \*TH Darmstadt, Institute of Applied Physics, Hochschulstraße 6, 64289 Darmstadt, Germany.

An experimental and theoretical study of the nonlinear optical properties of dye-doped liquid crystals in the isotropic phase is presented. In this system a novel mechanism for optical nonlinearity is acting which is analogous to that responsible for the large enhancement of the optical Freedericksz effect observed in the nematic phase [1]. Namely, a polarized laser pulse can create anisotropic populations of excited and ground state dye molecules. These populations then exert a net torque on the host molecules, inducing orientation and birefringence. This mechanism is very general and in principle it should be observable in every absorbing liquid.

[1] I. Jánossy, Phys. Rev. **E49**, 2957 (1994)

#### **B3.006**

NONLINEAR BLEACHING IN THE SELECTIVE REFLECTION OF NON-ABSORBING CHIRAL NEMATIC LIQUID - CRYSTAL THIN FILMS, S. Lukishova, K. Lebedev, E. Magulariya, S. Belyaev\*, A. Schmid\*\*, N. Malimonenko\*, Inst. of Radioengineering and Electronics of the Russian Acad. of Sci., 11 Mokhovaya, 103907, Moscow, Russia.;\*Organic Intermediates and Dyes Inst. (NIOPIK), Moscow, Russia; \*\*Lab. for Laser Energetics, Univ. of Rochester, 250 East River Road, Rochester, N.Y., 14623-1299, USA.

High-intensity, circularly polarized laser beams tuned to selective-reflection conditions in chiral-nematic liquid-crystal layers made possible the first observation of a light-induced drop in the chiral reflection coefficient of liquid-crystal layer both for free-space irradiation, and in laser resonator. The dependence of the effect on intensity (and its independence on average power density) permits one to connect it with the chiral nematic's helix pitch dilation up to spiral untwisting in the field of light wave. Up to now, this effect had been observed only in static and low-frequency electric and magnetic fields. A laser operational mode was used with picket fence of pulses to accumulate the helical pitch dilation. Nonlinear bleaching of the medium's reflectivity could be observed over time intervals that allowed a distinction in the driving mechanism of nonlinear bleaching between optical-field-induced and thermal processes.

# Shapes and dynamics of giant vesicles

## Udo Seifert

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Vesicles consisting of a bilayer membrane of amphiphilic lipid molecules are remarkably flexible surfaces that show an amazing variety of shapes of different symmetry and topology. Transitions between these shapes can be induced by changing temperature or by the action of optical tweezers.

Various examples will be given to illustrate the systematic physical theory developed to understand the static and dynamic aspects of vesicle configurations [1]. The preferred shapes arise from a competition between curvature energy, which derives from the bending elasticity of the membrane, geometrical constraints such as fixed surface area and fixed enclosed volume, and a signature of the bilayer aspect. These shapes of lowest energy are arranged into phase diagrams, which separate regions of different symmetry by continuous or discontinuous transitions. For vesicles of non-spherical topology, the conformal invariance of the curvature energy leads to conformal diffusion, which signifies a one-fold degeneracy of the ground state [2,3]. As an example for a dynamical shape transformation, the laser-induced pearling instability of tubular vesicles [4] will be explained using the concept of marginal stability [5,6].

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- [2] F. Jülicher, U. Seifert, R. Lipowsky, Phys. Rev. Lett. 71, 452, 1993.
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- [6] R. Goldstein et al, J. Phys. II France, May 1996.

#### C1.I01

ALIGNING EFFECTS IN NEMATICS DUE TO ANCHORING COMPETITION, A. L. Alexe-Ionescu, M. Giocondo, M. Iovane and <u>R.Barberi</u>, Istituto Nazionale di Fisica della Materia (INFM), Research Unit of Cosenza, Italy.

The interface properties of a nematic liquid crystal in contact with a solid substrate are investigated by considering the competition between alignment sources due to short and long range nematic-substrate interactions.

The effect of a destabilising long range anchoring source (planar) on a short range nematic-substrate interaction (homeotropic) is investigated by considering a position dependent external field localized close to the substrate. According to the value of the short range anchoring energy strength, the stable nematic state can be homeotropic, distorted or planar. An analysis of the correspondent surface transitions is presented. This approach allows also to describe nematic surface transitions due, for instance, to temperature or selective ion adsorption.

An analysis on the possibility to obtain an actual control of the nematic surface conditions is also made, with a comparison with experimental results.

#### C1.I02

SURFACE INDUCED BULK ALIGNMENT OF SMECTIC LIQUID CRYSTAL FILMS\*, X. Zhuang and Y. R. Shen, Department of Physics, University of California, Berkeley, CA94720-7300

Understanding the mechanism of surface induced liquid crystal (LC) bulk alignment is essential to the design of LC displays. We have shown earlier that the mechanism responsible for the bulk alignment of nematic LC films by rubbed polyimides is the short-range substrate-LC and LC-LC interactions that align the surface LC monolayer and subsequent layers in an epitaxial manner<sup>1</sup>. Here, we extend on the theoretical and experimental investigation to smectic LC films. We use the Landau-de Gennes formalism with an appropriate free energy to establish correlation between the orientational distribution of the surface LC monolayer and the bulk alignment in the smectic-A and smectic-C phases. Experimentally, the surface monolayer orientation is measured by optical second harmonic generation and the bulk alignment by ellipsometry. The bulk alignment calculated from the surface monolayer orientation agrees with the measured values. We found that besides the nematic correlation between molecules, the coupling between smectic and nematic ordering also plays important role in determining the bulk alignment. Investigation of the surface induced bulk alignment in the smectic C\* phase useful for the design of ferroelectric LC devices is currently underway.

1. X. Zhuang, L. Marrucci, and Y. R. Shen, Phys. Rev. Lett. 73, 1513, (1994)

\*Work supported by NSF Grant no. DMR-9404273

C1.003

# TEMPERATURE DEPENDENCE OF THE PRETILT ANGLE AND POLAR ANCHORING STRENGTH OF NEMATIC LIQUID CRYSTAL ALIGNED ON RUBBED SIDE CHAIN LIQUID CRYSTALLINE POLYMER.

V.N.Raja, S.W.Kang, J.S.Lee and J.C.Lee, Samsung Display Devices, R&D center, Korea-442-390.

We have investigated the temperature dependence of pretilt angle ( $\theta$ ) and the anchoring strength of nematic liquid crystal molecules aligned on substrates treated with side chain liquid crystalline polymer poly (4-cyanophenyl-4'-ethoxybenzoyloxy) acrylate (LCP100).  $\theta$  variation with temperature showed an unusual behavior by showing two stable values over the measured temperature range. As the temperature is increased  $\theta$  changed from one stable value to another. On cooling the sample from the isotropic phase  $\theta$  increased from zero to a second stable value and thereafter remained as a temperature invariant. The temperature dependence of orientational extrapolation length failed to show a critical divergence instead a very small increase on approaching the N-I transition. This indicates that the surface order parameter is quite strong and hence the polar anchoring energy weakens quite gradually.

C1.O04

EFFECT OF CHAIN CONFIGURATION ON BULK LIQUID-CRYSTAL ALIGNMENT, <u>H.M.Wu</u>, Y.M.Zhu, Z.H.Lu, and Y.Wei, National Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing 210096, P.R.China.

A uniform alignment of the liquid-crystal(LC) molecules in the non-addressed state is a prerequisite for most liquid-crystal displays (LCDs). Although the use of polymer materials as orienting layers is well accepted in LCD production process, rather little is understood about the detail configuration of polymer chains within the orienting layers and the related inducing effect onto the LC layer.

Based on some model systems, we have systematically investigated the effect of chain configurations on the bulk LC alignment. The present study is arranged into the following sections: 1) LC alignment of helical or horizontal polymer chains. 2) Homogeneous to homeotropic anchoring transition induced by the configuration change of polymer backbones. 3) Effect of the side groups of polymer chains on LC alignment. 4) Competition between the aligning effects of oriented polymer chains and regularly distributed grooves.

C1.005

MODELLING NEMATIC LIQUID CRYSTAL ALIGNMENT ON ASYMMETRIC SURFACE GRATING STRUCTURES, C.V. Brown, G.P. Bryan-Brown and D.G. McDonnell, Liquid Crystal Group, DRA Malvern, Great Malvern, Worcs WR14 3PS, UK.

Nematic continuum theory has been used to model the macroscopic origin of the pretilt for nematic liquid crystal alignment over an asymmetric grooved surface. Static director configurations have been calculated numerically using the discretised forms of the continuum equations. Two symmetries have been investigated: a hybrid cell with a grooved lower surface and a uniform pretilt at the upper surface, and an antiparallel configuration with surface grating structures on both the upper and lower bounding plates. The model reproduces the existence of two distinct alignment regimes, a low pretilt regime where the director field follows the contours of the grating and a high pretilt regime where the director field shows a characteristic defect structure. The energies of the distorted director field and the pretilt in the two regimes is determined by the parameters of the surface grating. For certain sets of grating parameters both alignment regimes are equally energetically favourable. The temperature dependence of the pretilt imparted by the surface and the effective zenithal anchoring energy are also predicted by the model.



## C1.006

THE NANOMETRIC SURFACE STRUCTURE OF SUBSTRATES USED FOR LIQUID CRYSTAL ALIGNMENT, <u>S.D.Haslam</u>, A.J.Pidduck, G.P.Bryan-Brown and J.C.Jones, Defence Research Agency, St. Andrew's Road, Great Malvern, Worcestershire, WR14 3PS, U.K.

The use of atomic force microscopy (AFM) to study low aspect ratio surfaces such as polymer layers has recently been established [for example, see reference 1]. Here we present a detailed study of polymer alignment films that could be used in liquid crystal devices, along with studies of some possible underlying layers in the device, such as the indium tin oxide layer and the barrier layer. This allows the relationship between the topology of the underlying layers and the surface structure of the final device to be investigated. The structures of the rubbed alignment films are then presented in detail. The role of each surface feature generated by rubbing is discussed in relation to the alignment of liquid crystals. Consequently, a possible mechanism for liquid crystal alignment can be inferred. These studies also suggest that the rubbing technique used to produce such plates is unnecessarily harsh and that polymer alignment may well be achieved by using less force.

1. J.Y.Huang, J.S.Li, Y.S.Juang and S.H.Chen, Jpn. J. Appl. Phys., 34, Part 1, No.6A, (1995), pp. 3163-3169

C2.I01

SURFACE TRANSITIONS, CRITICAL ADSORPTION, AND SPONTANEOUS POLARIZATION IN-VERSION IN FREELY SUSPENDED FILMS, <u>Ch. Bahr</u>,\* C.J. Booth,\* D. Fliegner,\* and J.W. Goodby<sup>†</sup>, \*Physical Chemistry, University Marburg, D-35032 Marburg, Germany; \*Physical and Theoretical Chemistry, Technical University Berlin, D-10623 Berlin, Germany; <sup>†</sup>School of Chemistry, The University, Hull HU6 7RX, England.

We present recent results concerning the smectic-A – smectic-C transition and the ferroelectric smectic-C phase in freely suspended films. The Sm-A – Sm-C transition, which occurs at the free surface of the compound under investigation, is, in contrast to earlier studies of the Sm-A – Sm-C transition [1] and other transitions [2], not restricted to the first smectic layer at the surface but extends over a surface domain characterized by a correlation length of about four layers. In very thick films, the thickness of the tilted surface domain grows in a divergence like behavior as the bulk Sm-A – Sm-C transition temperature is approached from above; the corresponding results are compared with the Fisher-de Gennes-model [3] of critical adsorption. The compound under investigation shows in its bulk ferroelectric Sm-C phase at a certain temperature a spontaneous inversion of the direction of the spontaneous polarization with respect to the direction of the molecular tilt. This phenomenon is found to be present also in thin films consisting of only few layers; our results support rather the competing-conformer model [4] of the polarization inversion than the dipolar-quadrupolar-coupling model [5].

- [1] S.M. Amador and P.S. Pershan, Phys. Rev. A 41, 4326 (1990).
- [2] see e.g.: B.D. Swanson, H. Stragier, D.J. Tweet, and L.B. Sorensen, Phys. Rev. Lett. 62, 909 (1989);
   R. Geer, T. Stoebe, and C.C. Huang, Phys. Rev. E 48, 408 (1993); and references therein.
- [3] M.E. Fisher and P.-G. de Gennes, C. R. Acad. Sci. (Paris), Ser. B 287, 207 (1978).
- [4] J.S. Patel and J.W. Goodby, Phil. Mag. Lett. 55, 283 (1987).
- [5] B. Urbanc and B. Žekš, Liq. Cryst. 5, 1075 (1989); R. Meister and H. Stegemeyer, Ber. Bunsenges. Phys. Chem. 97, 1242 (1993).

C2.I02

# SPONTANEOUS PERIODIC IN-LAYER DIRECTOR MODULATIONS IN TILTED CHIRAL SMECTICS

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It has been recognised that the chirality induces periodic in-layer band of director leading to the formation of the stripe and square net of the defect walles<sup>1</sup>. The corresponding textures have been detected in the free suspended films in SmC\*, SmC\*<sub>A</sub> and SmI\*<sub>A</sub> phases, in the temperature range where the usual twist-band-modulations along the layer normal (z-helix) vanish. This effect occurs in the vicinity of the z-helix twist inversion temperature. The distinctly different temperature behaviour of the pattern periodicity was found in SmC\*<sub>A</sub>, SmC\* and SmI\*<sub>A</sub> phase. Under electric field applied within the smectic layer the stripe pattern is stabilised against the square textures, the stripes becoming oriented perpendicular to the field direction. A model of the director field related to the textures with 1D and 2D symmetries is constructed and discussed.

E.Gorecka at al., Phys Rev.Lett., 75,4047, 1995

#### C2.O03

FERROELECTRIC COLUMNAR MESOPHASES OF PYRAMIDIC DISCOTIC LIQUID CRYSTALS, A. Jákli†, A. Saupe, G. Scherowsky\* and Xin Hua Chen\*‡, Max Planck Research Group, Liquid Crystal Systems, Mühlpforte 1, 06108 Halle/S, Germany, † present address: Research Institute for Solid State Physics, H-1525 Budapest, P.O. Box. 49, Hungary, \*Institut für Organische Chemie, TC2, Technische Universität Berlin, Straße des 17 Juni 124, 10623 Berlin, Germany; \*‡ present address: Condensed Matter Laboratory, Department of Chemistry, University of Colorado, Boulder, Colorado 80309

We synthesized and studied tris benzocyclononenes carrying six chiral side chains. They are pyramidic shaped molecules exhibiting columnar mesophases. A homeotropic alignment of the columnar liquid crystal was achieved by cooling the film between plates treated by octadecyl triethoxy silane in the presence of a D.C. field. Below the clearing point a transient optical effect was observed upon field reversal. Simultaneously there is a peak in the current flowing though the sample. These results indicate that the columnar phase is ferroelectric with a polarization along the columnar axis and the direction of the polarization can be reversed by electric fields. The time for polarization reversal is in the range of few seconds a few degree below the clearing point The magnitude of the maximum polarization calculated from the current peak is  $10\text{mC/m}^2$ , i.e. much larger than typical for polarization arising from chirality.

#### C2.O04

CHIRAL FLUCTUATIONS IN ACHIRAL PHASES, <u>Tom Lubensky</u>, Randall D. Kamien, and Holger Stark, Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, USA.

Chiral molecules tend to form phases with chiral structures such as the cholesteric phase, the blue phases, the TGB phases, and the smectic-C\* phase. However, they also form phases, such as the isotropic fluid, whose structure is achiral. In such structures, molecular chirality gives rise to thermal fluctuations that are chiral. Left-handed and right-handed twists occur with different probabilities and lead to a fluctuation-induced rotary power of light in addition to the rotary power of the individual molecules. We discuss this effect in a number of contexts, including the smectic-A phase, the twist-inversion point in the cholesteric and smectic-C\* phase, and lyotropic lamellar phases.

#### C2.O05

DISTINCT FERROELECTRIC SMECTIC LIQUID CRYSTALS CONSISTING OF ACHIRAL MOLECULES WITH BANANA SHAPE, T. Niori, T. Sekine, J. Watanabe, T. Furukawa\* and H. Takezoe\*, Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan, \*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan.

We synthesized a bent molecule and found that the smectic phase formed is biaxial with the molecules packed with the same bend directionality into a layer. Because of this characteristic packing, the spontaneous polarization appears parallel to the layer and the molecular bend plane, and is about  $50 \text{ nC/cm}^2$  independent of temperature. A large dielectric constant attributable to the so-called Goldstone mode was also observed. It is the first obvious example of ferroelectricity in achiral smectic phase which is ascribed to the  $C_{2\nu}$  symmetry of the molecular packing.

C2.O06

# DYNAMICS OF COLLECTIVE MODES IN FERROELECTRIC LIQUID CRYSTALS (FLCs) IN CONFINED GEOMETRY

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and

N. A. Clark Condensed Matter Laboratory, Department of Physics, University of Colorado, Boulder, Co., U.S.A.0

Two FLC-aerogel systems were investigated using dielectric spectroscopy over a temperature range for the chiral nematic, semctic A and smectic C\* phases. Both transitions (first order) from N\* to SmC\* and (second order) from SmA to SmC\* seen in the bulk FLCs [1] were found to be greatly broadened in the confined systems. The collective modes (Goldstone and Soft Modes) were detected in FLCs confined in aerogel pores. However the magnitude of the dielectric response was significantly reduced by the finite size effect. A wider distribution in the relaxation times in the confined systems was observed. This is caused by the ramdomness of the interactions between the director and the surfaces of pores [2]. The most interesting finding is an additional relaxation process clearly detected in the W314-aerogel system. This process is tentatively assigned to be due to the dielectric response of the molecules existing at the interface between the bulk FLC molecules and the surface of the pores.

[1] T. Bellini, N. A. Clark, L. Wu, C. W. Garland, D. Schaefer and B. Olivier, Phys. Rev. Lett., 69, 788 (1992).

[2] X. Wu, W. I. Goldburg, M. X. Liu and J. Z. Xue, Phys. Rev. Lett., 69, 470 (1992).

#### C3.I01

DENSITY-FUNCTIONAL THEORY FOR ELASTIC CONSTANTS OF LIQUID CRYSTAL, Yashwant Singh, Department of Physics, Banaras Hindu University, VARANASI-221 005, India

We develop a density-functional theory based on weighted density formalism to derive expressions for the elastic constants of liquid crystals. These expressions are written in terms of order parameters characterizing the nature and amount of ordering of the liquid crystal phases and the structural parameters which involve the spherical harmonic coefficients of the direct pair correlation function of an effective isotropic fluid, the density of which is determined using a criterion of the weighted density-functional formalism. We estimate the values of these structural parameters corresponding to different liquid crystalline ordering and use them to calculate the elastic constants of some mesophases. We compare our results with experiments wherever such data are available.

C3.102

# Elastic Theory of a Spatially Restricted Nematic Liquid Crystal

#### V. M. Pergamenshchik

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Continuum approach to liquid crystals has been developed for the infinite medium. However, presence of an actual surface explicitly breaks the symmetry of unrestricted bulk. There are two additional contributions to the free energy which emerge from the very presence of the surface and are related with the director: anisotropic surface tension and the so-called  $K_{13}$  and  $K_{24}$  energy terms which are of the form of total divergence. They give rise to novel mechanisms of spontaneous symmetry breaking of the director field which do not work in the infinite media. Moreover, ground state of the nematic director field which has conventionally been considered as uniform is predicted to be distorted close to the bounding surface. This, probably the most dramatic consequence of a spatial boundedness, is associated with the divergence  $K_{13}$  term.

Both the anchoring and inclusion of the  $K_{13}$  term in the standard elastic theory which are conventionally considered separately present problems. We show that both difficulties ("too strong anchoring and too strong surface derivative") are actually a single problem. The instability of the uniform director state and surface mode emerging is shown to be similar to the Goldstone effect. Similar to the way the Goldstone mechanism generates mass of the boson field, the  $K_{13}$  induced instability generates anchoring. We show that weak surface mode which can be incorporated in the standard elasticity theory generates weak dynamic anchoring. Depending on the sign of  $K_{13}$ , the dynamic anchoring favours a planar or homeotropic alignment.

Thus, the elasticity theory of restricted medium unifies elastic and anchoring phenomena via the Goldstone mechanism of mass generation. Basic equations of this theory which incorporates the  $K_{13}$  term are derived.

C3.O03

QUADRUPOLAR INTERACTION IN NEMATIC LIQUID CRYSTALS, <u>L. R.</u> Evangelista\* and S. Ponti, Dipartimento di Fisica, Politecnico di Torino, 10129 Turin, Italy.

A pseudo-molecular approach is used to investigate the effect of the quadrupolar interaction on the bulk elastic properties of nematic liquid crystals. It is shown that the quadrupolar interaction alone cannot give rise to the nematic phase. This conclusion follows from the result that all the elastic constants appearing in the elastic energy density, due to the quadrupolar interaction, are identically zero. The elastic energy density is evaluated by supposing the interaction volume of spherical and of ellipsoidal shape. In both cases the total elastic energy is zero and the total energy is reduced to the uniform part. The case of a phenomenological screened quadrupolar interaction is also considered.

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C3.O04

ELASTIC CONSTANTS OF BINARY MIXTURES OF UNIAXIAL NEMATIC LIQUID CRYSTALS, A. Kapanowski and K. Sokalski\*, Institute of Physics, Jagellonian University, Reymonta 4, 30-054 Cracow, Poland.

Correspondence between microscopic [1] and phenomenological [2] approaches to binary mixtures of uniaxial nematic liquid crystals is concerned. General microscopic expressions for the three bulk elastic constants and the two surface constants for uniaxial nematic phases are derived in case of a very weak anchoring and a small density. For a special class of potentials the elastic constants are expressed in terms of the order parameters and molecular parameters. The Nehring-Saupe relation between the bulk and surface constants is recovered for one and two component substances. As an example a mixture of prolate and oblate molecules is concerned. The dependence of the order parameters and the elastic constants on the composition is discussed. A discontinuous change of properties of the mixture is predicted.

- [1] A. Chrzanowska and K. Sokalski, Phys. Rev. E <u>51</u>, 2295 (1995).
- [2] S. Stallinga and G. Vertogen, Phys. Rev. E 49, 1483 (1994).
- \*Supported by the Polish Committee for Scientific Research Project No. 2P30216704.

C3.O05

#### DENSITY FUNCTIONAL THEORY OF SURFACE-LIKE ELASTIC CONSTANTS

Hiroshi Yokoyama, Molecular Physics, Electrotechnical Laboratory, Tsukuba, 305, Japan.

Since the introduction of surface-like elastic constants  $K_{13}$  and  $K_{24}$  by Oseen in 1933 along with the now established splay, twist and bend elastic constants of nematics, their nature and significance have arisen a long-lasting debate[1]. I show here based on the density functional formulation of the curvature elasticity that those surface-like elastic constants are in principle ill-defined in the sense that their values are not unique, but depend on the way the free energy functional is molded into a local free energy density. This subtlety in constructing a local thermodynamic function is well-known in statistical physics of ordinary liquids [2], but not so well recognized in liquid crystal field [3]. The present theory does yield interfacial free-energy contributions with the same symmetry as  $K_{13}$  and  $K_{24}$  terms, but the relevant interfacial elastic constants are no longer intrinsic properties of the liquid crystal.

- (1) See, for example, V.M. Pergamenshchik, Phys. Rev. 48, 1254(1993).
- (2) J.S. Rowlinson and B. Widom, Molecular Theory of Capillarity, Oxford Univ. 1982.
- (3) H. Yokoyama, Mol. Cryst. Liq. Cryst. 165, 265(1988).



C3.O06

FREEDERICKSZ TRANSITIONS IN A PLANAR NEMATIC CELL AND THE SURFACELIKE ELASTIC CONSTANT PROBLEM, A.D. Kiselev, and V.Yu. Reshetnyak\*, Department of Pure and Applied Mathematics, Chernigov Technological Institute, 250027 Chernigov, Ukraine.

On the basis of local stability analysis we have studied how the surfacelike elastic terms, that are known as the  $K_{24}$ -term and the  $K_{13}$ -term, influence Freedericksz transition in nematic liquid crystal (NLC) sandwiched between two parallel plates. Two cases are considered: (a) the homeotropic anchoring is favored at both walls and magnetic field is assumed to be parallel to the confining surfaces; (b) the boundary conditions are planar and the magnetic field is normal to the walls. As far as the usual homogeneous Freedericksz transition is concerned, the results are found to be quite different from those obtained in [1]. In particular, it is shown that the splay-bend term can lead to a discontinuous Freedericksz transition. In the case (b) the periodic splay-twist Freedericksz transition is investigated in the presence of the surfacelike elastic terms. The Pergamenshchik approach to the  $K_{13}$ -problem is discussed.

1. V.M. Pergamenshchik, P.I.C. Teixeira and T.J. Sluckin, Phys. Rev. E 48, 1265 (1993).

"This work is partially supported by NSF Grant U58000.

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C4.007

LIQUID CRYSTALS IN THE CLASSROOM, Rose Darling, Brimfield Elementary School, Kent, OH, 44240, USA.

This interactive session will present hands-on activities that teach basic scientific concepts essential to laying a solid foundation for the more complex ideas students will encounter in their lives. Both the properties and applications of liquid crystals are utilized to teach and tie in chemistry, physics, and math with language skills. Elementary Students' reactions and evaluations will be also be presented.

C4.O08

LIQUID CRYSTAL OUTREACH AND VISUAL AIDS, <u>Renata-Maria Marroum</u>, Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA.

ALCOM is dedicated to improving science education at all levels through its Education Outreach programs. The core effort of the K-12 programs is the development of liquid crystal-based instructional materials that focus on understanding basic scientific concepts and making current technology comprehensible. The unique and attractive properties of liquid crystals and their applications make them an effective medium for teaching science using an inquiry-based approach to learning. The visual aides and instructional materials used in the various outreach programs will be presented.

C4.O09

FROM THE CLASSROOM TO THE LABORATORY: A WAY OF INTRODUCING RESEARCH, Luz J. Martinez-Miranda, Dept. of Materials and Nuclear Eng., Univ. of MD, College Park, MD, 20742, USA, Dept. of Physics and Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA.

We present a simple approach to intorducing current research results to students based solely on principles and equations learned as part of the curriculum requirement. This method achieves two goals: a. making research accessible to students at the beginning of their course of studies; and b. illustrating the application of "textbook" concepts to current research. The presentations can be combined with demonstrations or hands on workshops when possible.

<sup>†</sup> Work supported partially by NSF grant No. GER-94-50118.

#### C4.O10

LIQUID CRYSTALS RESEARCH IN THE PHILIPPINES, DR. Z.B. DOMINGO, Liquid Crystals Laboratory, National Institute of Physics, University of the Philippines, Diliman, 1101 Quezon City, Philippines.

Liquid crystals research in the Philippines has taken off. With researches centered on three thrusts namely: LC Synthesis, Formulations and Biological Aplications, the Liquid Crystals Laboratory at the College of Science, University of the Philippines, is inter-disciplinary and supported by characterization and research facilities at the National Institute of Physics, Institute of Chemistry and Department of Molecular Biology and Biotechnology.

LC Synthesis utilizes local materials and has successfully produced cholesteryl esters with thermochromic

capabilities and polymorphism properties.

LC Formulations are made from commercially available products to PDLCs, CNDs and PDCLCs, with emphasis on encapsulation techniques to accelerate academe-industry partnership.

LC Biological Applications are focused on the determination and/or verification of LC properties of selected physiological membranes, as well as antimutagenicity studies using the Micronucleus Test and Bio-Assay Protocol.

The Liquid Crystals Laboratory in the Philippines has pioneered LC research in Southeast Asia. With possible organized regional linkages and ILCS support, it looks forward to a more dynamic, sustainable and interactive LC research in this part of the world. Indeed, LC research has come full circle.

#### C4.011

AN ELECTRONIC TEXTBOOK FOR POLYMER LIQUID CRYSTALS, <u>J. W. Graff</u>\*, J. L. Koenig\*\*, P. G. Cramer\*, W. L. Gordon\*, Department of Physics\* and Department of Macromolecular Science\*\*, Case Western Reserve University, Cleveland, OH 44106-7079.

A network-based electronic textbook is presented, providing a basic introduction at the college freshman level to the fields of polymers, liquid crystals, and polymer liquid crystals. This electronic textbook contains virtual laboratories, animations, audio and digitized video materials in addition to hypertext for use in self-instruction or as part of formal course. This project is a cooperative effort between the Department of physics and the Department of Macromolecular Science at Case Western Reserve University in connection with the ALCOM center.

Supported by NSF/S&TC Advanced Liquid Crystalline Optical Materials (ALCOM) under grant DMR 89-20147

LIQUID CRYSTAL SMART REFLECTORS, Robert B. Meyer, Ching-Chao Chang, and Franklin Lonberg, The Martin Fisher School of Physics, Brandeis University, Waltham, MA 02254-9110, USA.

We present results concerning the development of liquid crystal smart reflectors, consisting of a cholesteric liquid crystal with temperature sensitive helix pitch, in combination with a light absorbing dye. Light entering the liquid crystal is absorbed by the dye, generating heat which raises the temperature of the liquid crystal. The resulting change in the helix pitch of the cholesteric causes an increase in its reflectivity, reducing the intensity of light that can be absorbed by the dye. This negative feedback stabilizes the reflector for a given light intensity. The smart reflector thus achieves a reflectivity which increases with increasing intensity of incident light. We report on two configurations of the device, with both experimental measurements and mathematical models of the system. Performance of the experimental devices is discussed, including the crucial role of cholesteric defects. Problems of containment and alignment are discussed. Other versions of the smart reflector are discussed, in which temperature is not used as a control mechanism. Some comments are made on smart reflectors not based on cholesterics.

Research supported by the U.S. Army Research Office and the National Science Foundation.

D1.I01

STATIC AND DYNAMIC CRITICAL C<sub>p</sub> BEHAVIOR AT SMECTIC-HEXATIC TRANSITIONS, Zdravko Kutnjak and <u>Carl Garland</u>\*, Department of Chemistry and Center for Materials Science and Engineering, M.I.T., Cambridge, MA 02139, USA.

High-resolution ac calorimetry has been used to study  $C_p(\omega,T)$  for the SmC-SmI critical point in a racemic mixture of 8SI + 8OSI and the SmA-HexB second-order transition in 65OBC. Both systems exhibit critical dynamics near  $T_c$  with relaxation times that diverge like  $C_p$ . 8SI + 8OSI exhibits two relaxation modes and 65OBC exhibits three. In each case, for the lowest frequency mode the divergence of the real part of  $C_p$  is characterized by a critical exponent  $x \ge 1$  that seems to correspond to the susceptibility exponent  $\gamma$ . For 8SI + 8OSI,  $x = 1.06 \pm 0.08$  in agreement with the mean field value  $\gamma = 1$ ; for 65OBC,  $x = 1.32 \pm 0.07$  in agreement with the 3D-XY value  $\gamma = 1.316$ .

\*Supported by NSF Grant DMR 93-11853.

D1.I02

THE EFFECT OF CHIRALITY ON THE PHASE TRANSITIONS OF CHIRAL/8CB MIXTURES, G. lannacchione, S. Qian, M. Wittebrood, and D. Finotello\*, Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

We report on a study of mixtures of octylcyanobiphenyl (8CB) and equal amounts of two chiral agents (CE2 and CB15) as a function of chiral pitch (concentration). Bulk studies reveal a widening cholesteric temperature range with increasing chirality. The first order cholesteric-isotropic (CI) transition shifts marginally to lower temperature with increasing chirality while exhibiting a pre-transition feature near its C<sub>p</sub> maximum. The smectic-cholesteric (SC) C<sub>p</sub> anomaly becomes smaller and shifts to lower temperatures with increasing chirality and exhibits the unique feature of a discontinuous jump on the *low* temperature side of the C<sub>p</sub> peak. The increased chirality suppresses the smectic formation through twist elastic distortion. Upon anopore confinement, the C<sub>p</sub> maximum of the CI transition increases from bulk with the disappearance of the pre-transition feature while the SC transition becomes extremely rounded and suppressed. The transitions shift to lower temperatures while generally maintaining the bulk cholesteric temperature range. Preliminary deuterium NMR studies on anopore confined samples find a director conformation transition upon cooling into the smectic phase indicating a partial unwinding of the cholesteric pitch.

\* Supported by NSF-STC ALCOM Grant DMR 89-20147.

D1.003

PHOTOACOUSTIC AND PHOTOPYROELECTRIC MEASUREMENTS OF THE THERMAL DIFFUSIVITY AND THERMAL CONDUCTIVITY ANISOTROPY OF ORIENTED LIQUID CRYSTALS. J. Caerels, E. Schoubs and J. Thoen, Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium. Photoacoustic (PA) and photopyroelectric (PPE) techniques provide very sensitive tools for simultaneous measurements of the temperature dependence of static as well as transport quantities of small size liquid crystal samples [1]. From PA and PPE measurements, we obtained detailed information on the anisotropy of the thermal diffusivity  $\alpha$  and the thermal conductivity  $\kappa$  for compounds of the dialkylazoxybenzene (nAB) and alkylcyanobiphenyl (nCB) homologous series. In order to investigate the anisotropy in the thermal transport parameters between heat flow along and perpendicular to the director, the samples were aligned either with a magnetic field (for PA) or by surface treatment of the cell walls (for PPE) for homeotropic or planar alignment. The observed anisotropy in  $\alpha$  and  $\kappa$  is compared with theoretical predictions based on the length - width ratio of the constituent molecules. Results near the isotropic - nematic and nematic - smectic A transitions show the usual specific heat capacity anomalies but no critical effects are observed in the temperature dependence of the thermal conductivity.

[1] E. Schoubs, H. Mondelaers, and J. Thoen, J. Phys(Paris) C7,257(1994)

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D1.004

REAL-SPACE MEASUREMENT OF NEMATIC DIRECTOR FLUCTUATIONS TO PROBE THE NEMATIC-SMECTIC-A PHASE TRANSITION, <u>Anand Yethiraj</u> and John Bechhoefer, Dept. of Physics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.

The nature of the nematic--smectic-A (NA) phase transition in liquid crystals has for a long time been a contentious, unsolved problem in condensed matter physics. Landau theory predicts that the transition can either be first- or second- order, depending on material parameters. However nematic director fluctuations can make the transition very weakly first order. For materials whose nematic phase exists over a wide range of temperature, the fluctuations will be weaker at the NA transition. It is not known whether in such materials the transition is truly second order or just very weakly first order. Calorimetric measurements have measured latent heats at small nematic ranges but have found the transition to be indistinguishable from second order at larger nematic ranges. I will describe a new experimental technique we have used to investigate the NA transition. We have looked at 8CB (and two other materials) experimentally by measuring, using real-space imaging, the magnitude of nematic director fluctuations near TNA. Although the latent heat of 8CB is smaller than the resolution of the best adiabatic calorimeters, we observed a well-resolved jump as we cross the NA transition, demonstrating the sensitivity of this technique.

D1.005

EXPERIMENTAL STUDY OF THE DYNAMIC PROPERTIES OF THE N-SMA PHASE TRANSITION, P. Sonntag, D. Collin and P. Martinoty, Laboratoire d'ultrasons et de dynamique des fluides complexes, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex France.

We present a detailled study of ultrasound velocity and attenuation near the N-SmA phase transition in TBBA, allowing us to characterize the various mechanisms governing the critical dynamics, and to determine the critical relaxation time  $\tau$  above and below  $T_{AN}$ . The plot of the normalized attenuation  $\delta\alpha/\delta\alpha_c$  ( $\delta\alpha$  is the critical attenuation and  $\delta\alpha_c$  its value at the transition) as a function of  $\omega\tau$  shows that the experimental data taken at various frequencies and temperatures collapse onto a single curve, thereby establishing the existence of a dynamic scaling law. The evaluation of the three static exponents associated with the elastic constants A, B and C (which are deduced from the velocity anisotropy) and of the two dynamical exponents related to  $\tau$  and  $\delta\alpha_c$ , indicates that the transition is 3D XY with an influence, which is more or less marked depending on the observables considered, of the coupling between the order parameter and the director fluctuations.



## D1.006

UNUSUAL SHORT-RANGE ORIENTATIONAL ORDER IN THE ISOTROPIC PHASE OF CHIRAL SMECTOGENIC LIQUID CRYSTALS, Gil M. Barretto and Peter J. Collings,\* Department of Physics & Astronomy, Swarthmore College, Swarthmore, PA 19081, USA

Short-range orientational order in the isotropic phase of chiral nematogenic and most chiral smectogenic liquid crystals is similar. As the temperature is decreased in a region roughly 5 K wide above the transition to the isotropic phase, short-range orientational order increases asymptotically until long-range orientational order sets in at the transition. This behavior is described quite well by a simple Landau-deGennes free energy, and in chiral systems this short-range orientational order produces pretransitional optical activity. Some of the new chiral smectogenic compounds with smectic  $C_A$  and smectic Q phases exhibit optical activity in the isotropic phase that is very different. First, after heating into the isotropic phase, the optical activity takes several hours to reach values that are reproducible. Second, even after reproducible values are obtained, the optical activity remains appreciable almost 100 K above the transition to the isotropic phase. Measurements on various compounds and different chiral-racemic mixtures suggest a number of possible explanations for this behavior.

D1.I07

## STUDIES OF DEFECTS IN CONFINED LIQUID CRYSTALS

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The texture of a confined liquid crystal is determined by bulk effects (elastic constant anisotropy, chirality, and applied fields) in addition to surface effects (nature and strength of the boundary conditions and the confinement geometry). Usually it is topologically impossible to satisfy the requirements of these influences in a continuous manner and hence the texture incorporates one or more defects. If the external influences are gradually changed, the defect structure may also gradually change, with defects combining, splitting into other configurations, or vanishing completely. We describe several experiments in which textures in spheres and cylinders are subject to external fields or changing chirality, and show how the defects evolve. Although the evolution is often complex, we show how the topological rules governing conservation of defect strength are always obeyed.

**D1.I08** 

# Optical Kerr Effect Measurements of Orientational Dynamics of Cyanobiphenyls Confined to Nanoporous Random Matrices

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Optical Kerr effect experiments on a sub-ps to  $\mu s$  timescale are used to investigate the reorientational dynamics of cyanobiphenyls confined to porous sol-gel glasses over a large temperature range in the isotropic phase and around the isotropic-nematic phase transition. Samples with a range of pore diameters (25-100 Å), different pore surface polarity and different chain length of the mesogen (5CB and 8CB) are employed. The respective influence of geometrical restriction and surface interaction is elucidated, contributing to the ongoing discussion about a description of the isotropic-nematic phase transition in confinement in terms of modified Landau-deGennes models, finite-size scaling, surface-induced order and random-field theories.

# D1.009

DIELECTRIC RELAXATION OF NEMATIC LIQUID CRYSTALS CONFINED IN POROUS MATRICES, <u>Ghanshyam P. Sinha</u> and Fouad M. Aliev, Department of Physics and Materials Research Center, University of Puerto Rico, San Juan, PR 00931-3343, USA.

We have investigated the dielectric properties of polar nematic liquid crystals (LC) confined in porous matrices. The porous matrices that were used had different structures - matrices with cylindrical pores in parallel orientation as well as matrices with random porous structure (average pore size ranging from 100 A up to 2000 A and pore volume fraction 3 % - 50 %). We found that the spatial confinement and the existence of a highly developed interface have a strong influence on the dielectric properties of confined LC. A new property that was observed for LC in both porous structures was the presence of a slow relaxational process (at frequencies < 100 Hz), which does not exist in the bulk. We also observed that at temperatures about 30 degrees below the bulk melting temperature, the dielectrically active modes were not completely frozen. This property was newly observed and is very different from the behavior expected in the solid phase. In order to explain the appearance of low frequency relaxational process and high values of dielectric permittivities of polar liquid crystals in pores, we need to involve theories of surface polarization and surface order electricity. This work was supported by US Air Force grant F49620-95-0520 and NSF grant OSR-9452893.

D2.I01

LAYER COUPLING FOR MOLECULAR ORIENTATION IN THE FIELD IN-DUCED ANTIFERROELECTRIC-FERROELECTRIC LIQUID CRYSTAL PHASE TRANSI-TION, <u>Sin-Doo Lee\*</u>, Jae-Hoon Kim, and Ju-Hyun Lee, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

We report on the layer coupling for the electric field induced ferroelectric ordering in antiferroelectric liquid crystals (AFLCs). AFLCs have a layer structure in which the herringbone formation of the molecular orientation in successive layers undergoes a helical rotation. On approaching the field induced antiferroelectric-ferroelectric (AF-FO) transition, the electro-optic response reaches a maximum and then decreases slowly with increasing the electric field. Moreover, the associated relaxation time exhibits two sharp peaks, indicating the existence of an intermediate ferrielectric-like (FE) phase between them. The anomaly observed is described terms of layer correlations in a simplified model which contains interactions of both the nearest (N) and next nearest (NN) neighboring layer pairs. The coupling constants for the N and NN neighboring layers are estimated. The relative strength between the two coupling constants is found to play an important role in molecular switching during the AF-FO phase transition. The static and dynamic features of the AF-FE-FO transition are also discussed in view of the available data.

\*Supported in part by Korea Science and Engineering Foundation through RCDAMP at Pusan National University.

D2.I02

MOLECULAR ORGANIZATION AND SPONTANEOUS POLARIZATION IN SMECTICS, D. J. Photinos, Department of Physics, University of Patras, Patras 26110, Greece.

It has recently been shown [1] that the tilted arrangement of common smectogens inevitably gives rise to polar ordering in the direction perpendicular to the tilt plane. The key factor for the appearance of such indigenous polarity is the characteristic structure of these molecules i.e. flexible chains *linked at an angle* to the elongated mesogenic core. Molecular dipoles and chirality are not essential to the polar ordering but only to its manifestation in the form of electric polarization. The general implications of this new theory as well as some of its quantitative inferences are presented and tested against measurements of spontaneous polarization (both in pure ferroelectric  $S_C$  phases and in nonchiral  $S_C$  host phases doped with chiral guest molecules), NMR measurements of segmental order parameters, dielectric relaxation studies in the microwave regime and Fourier transform infrared spectroscopy.

[1] D.J. Photinos and E.T. Samulski, Science, 270, 783 (1995).

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D2.O03

#### REVERSIBLE PROPAGATING FINGERS IN AN ANTIFERROELECTRIC

LIQUID CRYSTAL\*; Jian-feng Li, Xin-Yi Wang, Erik Kangas, P.L. Taylor, <u>Charles Rosenblatt</u>, Dept. of Physics, Case Western Reserve Univ., Cleveland, Ohio 44106 USA; <u>Yoshi-ichi Suzuki</u>, Showa Shell Sekiyu Kabushiki Kaishi, Kanagawa-ken, Japan; and P.E. Cladis, AT&T Bell Laboratories, Murray Hill, N.J. 07974 USA

Propagating finger-like solitary waves are observed in an antiferroelectric liquid crystal on application of an electric field greater than a characteristic threshold field  $E_{th}$  [1]. On reducing the field below  $E_{th}$  the fingers recede, also as solitary waves. The velocity of the waves, which to our knowledge is the fastest observed for a liquid crystal, scales approximately as  $E - E_{th}$  for  $E_{th}$  near  $E_{th}$ . A simple model, which includes a layer-layer coupling term, is presented which describes much of the observed behavior.

[1] J.-F. Li, X.-Y. Wang, E. Kangas, P.L. Taylor, C. Rosenblatt, Y. Suzuki, and P.E. Cladis, Phys. Rev. B 52, R13075 (1995)

D2.O04

INVESTIGATION OF FIELD INDUCED "DEVIL'S STAIRCASE" IN AFLC BY HIGH-FREQUENCY DIELECTRIC SPECTROSCOPY. Yu. P. Panarin. O. E. Kalinovskaja, J. K. Vij, Dept. of EEE, Trinity College, Dublin, Ireland.

The sample under investigation possess the following phase sequence:  $SmC_A$ - $SmC_Y$ -AF- $SmC^*$ -SmA. The unusual dielectric behaviour in  $SmC^*$  phase (the existence of two relaxation processes: ferro- and ferrielectric) have earlier been reported  $^1$ . Application of dc voltage causes the appearance of quasi-stable uniform state with value of macroscopic polarization varying from 65 to 80% of  $P_S$ . In addition to polarization and conoscopic investigation we used the high frequency  $\beta$ -relaxation around long molecular axis to identify the internal structure of this state. The cells of different thicknesses (8, 20, 50 and 100  $\mu$ m) were used to investigate the influence of the surface on structure. In a thin cell (8  $\mu$ m) the ferrielectric phases are suppressed by the surface and for thicker cells (>20  $\mu$ m) the electrooptical and dielectric properties are independent of cell thickness. The experimental results could be explained by the simultaneous existence of an unstable ferrielectric phase together with ferroelectric one within in  $SmC^*$ .

[1] Yu.Panarin, H.Xu, S.MacLughadha, J.K.Vij et al, J.Phys.: Condens. Matter, 7, L351 (1995).

D2.O05

DEUTERON NMR OF FERROELECTRIC AND ANTIFERROELECTRIC LIQUID CRYSTALS, R. Blinc and D. Abramič, J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia, M. Neubert and S. Keast, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA.

The temperature and angular dependence of the deuteron NMR spectra of the partially deuterated ferroelectric liquid crystal CE8 and the partially deuterated antiferroelectric liquid crystal MHPOBC have been studied. The results allow for a microscopic determination of the polar  $\langle\cos\phi\rangle$  and quadrupolar  $\langle\cos2\phi\rangle$  order parameters. The obtained data show that over most of the ferroelectric smectic C\* phase the quadrupolar order parameter  $\langle\cos2\phi\rangle$  is significantly larger than the polar order parameter  $\langle\cos\phi\rangle$ . In the vicinity of the smectic A to smectic C\* transition on the other hand the polar order is much larger than the quadrupolar one. The results seem to be in good agreement with the theoretical predictions [1]. This seems to be the first microscopic determination of the quadrupolar order in a ferroelectric liquid crystal.

[1] B. Urbanc, B. Žekš, Liq. Cryst. 5, 1075 (1989).

<sup>\*</sup> Supported by the NSF under Grant DMR-9502925 and by the Petroleum Research Fund



## D2.O06

SURFACE INDUCED TRANSITION FROM ANTIFERROELECTRIC PHASE TO FERROELECTRIC SMECTIC C\* ONE, A.L.Andreev, I.N.Kompanets, <u>E.P.Pozhidaev</u>, P.N.Lebedev Physical Institute, Leninsky pr. 53, Moscow 117924, Russia.

Antiferroelectric properties of liquid crystal mixtures consisting of some 5-n-alkyl-2(4-n-alkoxyphenyl)-pyrimidines[1] and some diesters of 4,4"-terphenyl dicarboxylic acid[2] were observed by us in LC layers of more than 50 mkm thickness at supplied voltage frequency  $10^{-4}$ - $10^{-3}$  Hz. These mixtures at the same frequency and 2-10 mkm layer thickness possess ordinary smectic C\* phase. Energy parameters of this surfase induced transition and corresponding D-E hysteresis loops as well as optical ones were investigated at different boundary conditions. Multistability and gray scale generation in both antiferroelectric and ferroelectric smectic C\* phases were considered also.

[1]. H.Zaschke, H.Schubert, F.Kuschel, D.Demus, **DD WP 95892** (1971), [2]. M.Loseva, N.Chernova, A.Rabinovich, E.Pozhidaev, J.Narkevich, O.Petrashevich, E.Kazachkov, N.Korotkova M.Schadt, R.Buchecker, Ferroelectrics, **114**, 357-377 (1991),

D2.I07

OPTICAL REORIENTATION IN DYE-DOPED NEMATICS, Enrico Santamato, Dipartimento di Scienze Fisiche, Pad. 20, Mostra d'Oltremre, 80125 Napoli

Recent experimental investigations showed that small amounts of dyes added to the pure nematic host can induce an amplification of the optical torque by about two orders of magnitude and even reverse its sign<sup>1,2</sup>. Experiments prove that this effect, nowadays known as Jánossy effect, is based on some yet unclear molecular interaction between the dye molecules and the nematic host. Recently, it was suggested that the effect may arise because of the difference in the interaction energy of the excited and ground-state dye molecules. We realized a series of experiments to investigate more deeply the dye-nematic interaction, including measurements of the optical torque in different dye-nematic mixtures (changing both guest and host) and time resolved fluorescence measurements to probe the excited state of the dye molecules.

- 1. I. Jánossy, L. Csillag, and A. D. Lloyd, Phys. Rev., A44, 8410 (1991);
- 2. I. Jánossy, Phys. Rev., E49, 4 (1994).
- \* Supported by INFM and CNR coordinated project.

**D2.I08** 

## LIQUID CRYSTAL REORIENTATIONAL DYNAMICS: RECENT DEVELOPMENT OF TIME-RESOLVED FT-IR AND POLARIZATION-MODULATED ELLIPSOMETRY

Hirokazu Toriumi, Department of Chemistry, The University of Tokyo Komaba, Meguro, Tokyo 153, Japan.

Knowledge concerning the elementary molecular processes of field-induced reorientational transition of liquid crystals is of key importance towards further detailed understanding of their dynamic behavior and the development of liquid crystal display devices. In this paper we describe the most recent advances in FT-IR time-resolved spectroscopy with sub-microsecond time resolution (FT-IR TRS), two-dimensional infrared frequency correlation spectroscopy (2D IR) and polarization-modulated ellipsometry (PME). These techniques can provide information about segmental transition dynamics and its depth-dependent variation: PME with 10-20 nm thickness resolution is particularly powerful in analyzing the behavior of surface anchoring layers. Advantages of using dynamic, polarized spectroscopy in the study of liquid crystal transition dynamics will be demonstrated for various examples.

# D2.O09

TIME-RESOLVED X-RAY STUDIES OF LAYER BEHAVIOUR DURING OPERATION OF A FERROELECTRIC DEVICE,

H.F. Gleeson and A.S. Morse, Department of Physics and Astronomy, Manchester University, Manchester M13 9PL, United Kingdom.

Time resolved small angle x-ray diffraction experiments have been undertaken for the first time throughout the switching cycle of a ferroelectric liquid crystal device. The x-ray data show that during switching with a low electric field the chevron structure adopted by the layers distorts, changing the chevron angle. Further, a rotation of the layers in the plane of the device is observed, coincident with the change in chevron angle. The motion of the layers takes place on a ten microsecond time scale and the angular rotation of the layers is approximately 1°.

D3.I01

OPTICS OF SOME CHIRAL LIQUID CRYSTALS, K.A. Suresh, Raman Research Institute, Bangalore 560 080, India.

Although the optics of chiral systems like cholesterics has been studied for well over one hundred years, the subject is still very relevant in view of new and different chiral systems that have been realised in the laboratory in recent times. These systems are associated with novel optical properties and have drawn considerable attention.

In this talk, we consider the optics of ferrocholesterics, chiral smectic C [1], absorbing cholesterics [2], absorbing and non-absorbing twist grain boundary smectics (TGBS) and some soliton lattices [3]. In particular, we deal with reflection, transmission and diffraction properties in these systems.

Further, we highlight some of the recent interesting results that have been obtained by us: 1) Asymmetric transmission along the twist axis in ferrocholesterics. 2) Modulations in the diffracted intensity in chiral smectic C. 3) Polarisation sensitive non-Bragg reflections in absorbing cholesterics. 4) Unusual reflection spectra and asymmetric diffraction in TGBS and finally (5) asymmetric reflections in defect lattices.

- [1] K.A. Suresh, Y.Sah, P.B.S. Kumar and G.S. Ranganath, Phys.Rev.Lett, 72, 2863 (1994).
- [2] Y.Sah and K.A.Suresh, J.Opt.Soc.Am. A11, 740 (1994).
- [3] G.S.Ranganath, N.Andal and K.A.Suresh, Optics of some absorbing defect lattices, this conference.

D3.I02

# NONLINEAR DIELECTRIC SUSCEPTIBILITY IN BLUE PHASES OF CHIRAL LIQUID CRYSTALS

Lech Longa<sup>1</sup>, Marta Zelazna<sup>1</sup>, and Hans-Rainer Trebin<sup>2</sup>

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Blue Phases of chiral liquid crystals have puzzled researchers for more than a century now. In particular, the structure of BPIII and the anomalous electrostiction of BPI await elucidation [1,2]. Standard theories of Blue Phases based solely on an expansion of the free energy in powers of the alignment tensor are not able to explain the experimental observations. It has been demonstrated by Pierański et al., that Cubic Blue Phases possess a strong nonlinear dielectric susceptibility (NDS). We have generalized the theory of cubic Blue Phases to incorporate the NDS tensor into the free energy expansion. Next, using this theory, we have investigated the distortion of the Cubic Blue Phase lattices by a weak electric field and determined the electrostriction tensor. It is found that there exists a range for the coupling strength between the alignment tensor and the cubic part of the nonlinear dielectric tensor where the anomalous electrostriction is predicted for BPI, in accordance with experiment. Thus bond orientational order seems to provide a link between two unsolved problems: that of the anomalous electrostriction of the Blue Phase I and that of the structure of the Blue Phase III.

- [1] See e.g. (a)Z. Kutnjak, C. W. Garland, J. L. Passmore and P. J. Collings, Phys. Rev. Lett. 74, 4859 (1995); (b)L. Longa, H.-R. Trebin and J. Englert, Cambridge University Press (in print). (c)J. Englert, L. Longa, and H.-R. Trebin, Liquid Crystals (in print). (d)T. C. Lubensky and H. Stark, Phys. Rev. E 53, 714 (1996).
- [2] L. Longa, M. Zelazna, H.-R. Trebin and J. Moscicki, Phys. Rev.E (in print).

## D3.O03

OPTICAL ACTIVITY OF A FLEXOELECTRICALLY-DEFORMED SMALL-PITCH CHO-LESTERIC LIQUID CRYSTAL, P. Galatola, Dipartimento di Fisica, Politecnico di Torino, I-10129 Torino, Italy.

By a Bloch-waves decomposition, we develop a general expression for the effective dielectric tensor of a small-pitch periodic dielectric medium. We apply this general formula to the case of a cholesteric liquid crystal, deformed by a flexoelectrical torque induced by an electric field orthogonal to the helical axis. As it is well known, the helical structure of a cholesteric liquid crystal can be unwound by an applied electric field, due to the dielectric coupling. Some time ago [1] it has been shown that a flexoelectrical torque induces a rotation of the plane of rotation of the cholesteric around the direction of the applied field. For small distortions, the rotation is linear in the applied field. Here we show that in the distorted structure, a spatial dispersion of the effective dielectric tensor arises, giving a rotatory power that scales as the ratio between the pitch of the cholesteric and the vacuum light wavelength. Generalizations of this result are discussed.

[1] J. S. Patel and R. B. Meyer, Phys. Rev. Lett. 58, 1538 (1987).

## D3.O04

THE USE OF THE DECYL ESTERS OF AMINO ACID HYDROCHLORIDES AS CHIRAL DOPANTS IN THE FORMATION OF AMPHIPHILIC CHOLESTERIC LIQUID CRYSTALS,

K. Radley\*, N. McLay and K. Gicquel, Department Chemical and Biological Sciences, The University of Huddersfield, Queensgate, Huddersfield, HD1 3DH, England.

Some of the hydrochlorides of amino acid decyl esters are assessed as chiral dopants in the formation of amphiphilic cholesteric liquid crystals using various achiral hosts. The amino acids used were serine, alanine, methyl cystein, methionine, and leucine. The achiral detergents were various N-methylated N-alkyl ammonium bromides. The sense and magnitude of the induced twist with each chiral dopant were found to be host dependent. It was thought the twist was the result the occurrence of the trans and cis rotamers in the C-O bond, where each rotamer makes an opposite but not equal contribution to the total twist<sup>1</sup>. This was confirmed using <sup>13</sup>C NMR, which was used to determine the relative populations of the rotamers. The results showed the twisting power to be a function of the rotamer ratio(linear progression) except in the case of the serine ester where the twisting power was found to be nearly independent of the rotamer ratio. The serine ester gave unusual results, that were thought to be due to the strong non-chiral interactions with the chiral micelle surface, which dissipate the chiral molecular interactions.

1. P. Styring, J. D. Vuijk, I. Nishiyama, A. J. Slaney and J. W. Goodby, J. Mat. Chem. 3 399 (1993).

#### D3.005

DIELECTRIC RELAXATION IN DIPOLE-DIPOLE INTERACTION SYSTEM, K. Moriya, \*S. Sugimori, \*\*K. Toriyama and \*\*D. A. Dunmur, Dep. of Chem., Fac. of Engineering, Gifu Univ., Yanagido, Gifu 501-11, Japan, \*Dep. of Industrial Chem., Toyama College of Technology, Hongoumati, Toyama 939, Japan, \*\*Centre for Molecular Materials and Dep. of Chem., Univ. of Sheffield, S3 7HF, UK

The dielectric constants of 1-cyano-2-fluoro-4-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene (CP1) and 1,2-difluoro-4-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene(CP3) were observed in the non-dipolar namatic liquid crystal solvent (1-[trans-4-ethylcyclohexyl]-2-[4-ethyl-2-fluorobiphenyl]ethane(I22) in different 5 concentrations in the frequency range from 1 kHz and 10 MHz. All solutions exhibited a low-frequency relaxation associated with end-over-end reorientation of the polar solutes in the ordered environment. The results indicated that the dipolar interactions in the CP1 solutions are qualitatively different from those for CP3 solutions. In particular, the dielectric properties of CP1 solutions can be interpreted by assuming that solute molecules are locally ordered antiferroelectrically, while for CP3 solutions the local order appears to be ferroelectric.[1]

[1] K. Toriyama, S. Sugimori, K. Moriya, D. A. Dunmur and R. Hanson, J. Phys. Chem., 100, 307 (1996).

D3.O06

ATOMIC FORCE MICROSCOPY ON THE FREE SURFACE OF FROZEN DISCOTIC CHOLESTERIC BLUE PHASES, M. Thieme, A. Hauser, A. Saupe, D. Krüerke\* and G. Heppke\*, Max-Planck-Arbeitsgruppe Flüssigkristalline Systeme, Mühlpforte 1, D-06108 Halle;(\*) Iwan N. Stranski Institute, Technische Universität Berlin, Sekr. ER 11, Straße des 17. Juni 135, D-10623 Berlin

Using cellobiose derivatives as chiral dopants in a discotic nematic host, discotic cholesteric phases with extremely small pitches were produced and it has been established that such binary mixtures tend to form up to three distinct blue phases [1]. A characteristic property of these mixtures is the occurrence of a glass-like state, allowing to freeze the liquid crystalline structure. Microscopic studies, reflection spectra, and Kossel diagrams all indicate that the three discotic blue phases BP<sub>D</sub>I, BP<sub>D</sub>II and BP<sub>D</sub>III behave similarly to the well known calamitic modifications. We report on the surface imaging of frozen Blue Phases in this low molecular mass discotic liquid crystal system with atomic force microscopy.

[1] D. Krüerke, H.-S. Kitzerow, G. Heppke and V. Vill, Ber. Bunsenges. Phys. Chem. 97 (10) 1371 (1993)

D3.I07

LYOTROPIC LIQUID CRYSTALS UNDER COUETTE AND OSCILLATORY SHEAR, Joseph T. Mang, MLNSC, Los Alamos National Laboratory, Los Alamos, NM 87545-1663 USA and Satyendra Kumar, Dept. of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 USA.

The small angle neutron scattering (SANS) technique has been utilized to investigate the flow properties of the discotic micellar isotropic (I), nematic (N) and lamellar ( $L_{\alpha}$ ) phases in aqueous solutions of cesium perfluoro-octanate. Under simple shear, no preferred orientation was observed in the I phase. The N phase was found to align with the nematic director in the direction of the shear gradient velocity, in agreement with the prediction of Carlsson 1, providing the first evidence for a positive value of the Leslie viscosity parameter,  $\alpha_2$ . The  $L_{\alpha}$  phase oriented with lamellae parallel to the shear plane. A reorientation of the director near the N- $L_{\alpha}$  transition was witnessed upon cooling from the N phase at a constant shear rate and is attributed, primarily to a change in the value of  $\alpha_2$  as a result of increasing lamellar correlations in the nematic phase. In contrast to simple shear, the application of oscillatory shear induced significant shifts in the phase boundaries, including nematic-like order some 7 K into the quiescent I phase which is attributed to a damping of critical fluctuations. The observed flow behavior will be compared to the flow properties of rod-like molecules.

[1] T. Carlsson, Mol. Cryst. Liq. Cryst. 89, 57 (1982).

## D3.008

UNUSUAL FEATURES OF THE SHEAR VISCOSITY BEHAVIOUR IN LYOTROPIC LIQUID CRYSTALLINE POLYMERS, C.R. Leal, M.T. Cidade and A.F. Martins, FCT-Dept. Ciência dos Materiais, Universidade Nova de Lisboa, P-2825 Monte da Caparica, Portugal.

The steady shear viscosity behaviour of a number of lyotropic liquid crystalline polymer (LCP) systems has been studied in function of the shear rate  $(\dot{\gamma})$ , for different values of the polymer molecular mass (M), concentration (c), and temperature (T), and the experimental data interpreted in terms of the continuum theory for LCP's recently proposed by Martins [1]. The circumstances under which one observes one, two, or three flow regions are rationalized. The theory also explains a number of unusual features so far observed with some LCP systems, including the following: i) an "hesitation" in the shear thinning region of the  $\eta(\dot{\gamma})$  curve; ii) a crossover, at some shear rate, of the curves  $\eta(\dot{\gamma})$  for two different polymer molecular masses (at a given c), and for two different temperatures or concentrations within certain ranges of these variables. At high shear rates  $\eta$  decreases (strikingly), with increasing M, although at low shear rates it increases with M, as usual. For the same physical reason, the crossover of the curves  $\eta(\dot{\gamma})$  for different temperatures implies that  $\eta$  decreases with T at high shear rates, as usual, but increases with increasing T at low shear rates. The curves  $\eta(\dot{\gamma})$  for different concentrations can all be reduced to a master curve through appropriate scalling.

[1] A.F. Martins, in Liquid Crystalline Polymers, ed. by C. Carfagna, Pergamon Press, U.K., 1994.

# D3.009

SHEAR INDUCED INSTABILITIES IN NEMATICS, T. Börzsönyit, A. Krekhovt, Á. Bukat, and L. Kramert, † Research Institute for Solid State Physics, H-1525 Budapest, P.O.B.49, Hungary, † Institute of Physics, University of Bayreuth, D-95440 Bayreuth, Germany

The response of a homeotropically aligned nematic liquid crystal to oscillatory rectilinear shear was studied experimentally and theoretically. The upper plate of the nematic cell oscillates in its plane, while the lower one is fixed. The frequency range  $0.1..100\ Hz$  has been studied in details.

- ullet In the small-amplitude regime, where  $A/d\ll 1$  (A is the amplitude of the upper plate oscillations, d is the nematic sample thickness) the director motion induced by the oscillatory shear has been followed optically. The frequency dependence of the phase shift between the optical response and the excitation was measured and the theoretical analysis was carried out.
- When the amplitude of oscillations is increased  $(A/d \approx 1)$  above a critical value pattern formation was observed. A roll pattern with optical features similar to that observed in EHC in nematics was found. It consists of stationary rolls with their axis perpendicular to the shear direction. The onset of the instability depending on the flow frequency and the cell thickness was studied and compared with the results of linear stability analysis.

## D3.O10

# SHEAR EXPERIMENTS ON A SIDE-CHAIN LIQUID CRYSTAL POLYMER: Determination of the polymer conformation and liquid crystal structure

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We consider the effect of shear on the structure and the conformation of the main-chain of a side-chain liquid crystal polymer. The change of structure and conformation is observed in situ by small-angle neutron scattering following two scattering planes respectively parallel to the shear plane and parallel to the vorticity plane. We find that, in the isotropic and the nematic phases, the main-chain dimensions in the shear plane are invariant within the shear range studied. In the smectic phase, however, the main-chain is elongated in the direction of the shear flow. In addition, the observation in the vorticity plane shows that the shear produces the orientation of the smectic layers parallely to the shear plane. It can be concluded that the polymer main-chain already confined between the mesogen layers by the smectic phase, is in addition stretched in the shear direction. These experiments are the very first results concerning the conformational behaviour of liquid crystalline polymers under shear.

# **Microconfined Liquid Crystals**

#### S. Žumer

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The term microconfined liquid crystals stands for systems which are severely confined to matrices of usually nontrivial geometry. Since the discovery of polymer dispersed liquid crystals about 10 years ago the interest in this subject is still constantly growing. Initial interest in spherical droplets has spread to liquid crystals confined by cylindrical cavities, porous glass, aerogels, polymer networks, etc. In parallel the interest in general surface phenomena in liquid crystals like orientational wetting and anchoring, surface viscosity, surface polarization, subsurface deformations etc. has grown as well. The following review reports on our recent advances in several aspects of microconfined liquid crystals:

#### Molecular modeling:

Simple molecular modeling of the nematic-solid interface using van der Walls and steric interactions help us to
understand what kind of subsurface deformations (usually associated to the K<sub>13</sub> elastic constant) can occur and
how they relate to the anchoring strength.

#### Surface induced paranematic ordering:

- NMR is particularly useful for the investigation of microconfined systems. A line shape study of the surface induced paranematic ordering demonstrates two wetting transitions as the length of the surfactant tail is changing. Low frequency NMR relaxation of such partially oriented layers is investigated to clearly point out the contributions of surface molecular exchange, surface diffusion and fluctuations in the surface layer.
- Collective orientational fluctuations in the inhomogeneously ordered nematics are investigated. Particular attention is paid to the effect of defects and surfaces. In a planar paranematic surface layer a description based on the tensor order parameter fluctuations allows for a separation to director, biaxiality and order modes and thus yield a complete description of the orientational fluctuations in such inhomogeneous system. Close to the ordering or structural transitions soft modes associated to the relevant component of the order parameter exhibit pretransitional slowing down [1].
- Recent AFM studies [2] stimulated the modeling of the forces in the inhomogeneously ordered nematic using a simple planar layer. Characteristic pretransitional increase and hysteresis effects are pointed out.

#### Nematic, chiral nematic and smectic structures:

- Using modeling of nematic structures it is demonstrated that a possible tilt on the nematic-air interface can be detected from a polarization microscope picture of a capillary half filled by a nematic liquid crystal [3].
- A systematic study of possible chiral nematic structures in a cylindrical cavity reviled that depending on the chirality and K<sub>24</sub> elastic constant the most stable are xy or xz double twisted structures.
- Radial, chevron, and hybrid smectic structures in cylindrical cavities described on the base of the Landau de
  Gennes approach are used to analyze the available experimental data. A similar approach is used to
  demonstrate how a local variation of the surface induced pretilt can nucleate a defect in the chevron direction in
  surface stabilized ferroelectric liquid crystal cells [4].
- [1] See also the contribution by P. Ziherl and S. Žumer
- . [2] See also the contribution by I. Muševič, J. Slak and R. Blinc
- [3] See also the contribution by M. Slavinec, S. Kralj, and S. Žumer
- [4] See also the contribution by S. Kralj and S. Žumer

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E1.I01

CALORIMETRIC AND OPTICAL REFLECTIVITY STUDIES OF THIN FREE-STANDING LIQUID-CRYSTAL FILMS, <u>T. Stoebe</u> and C. C. Huang, University of Minnesota, Minneapolis, MN, 55455, USA.

A unique experimental system capable of simultaneously measuring both the heat capacity and optical reflectivity of very thin free-standing liquid-crystal films has been developed. This system has been used to investigate phase transitions exhibited by a variety of compounds in smectic films ranging from hundreds down to only two molecular layers ( $\approx 50 \text{ Å}$ ) in thickness. The data obtained reveal an intriguing sequence of continuous transitions apparently localized to individual layers and provide insight into surface induced molecular order. The progression of this layer-by-layer transition can be understood in terms of a simple wetting model and is consistent with the layers interacting primarily via van der Waals-like forces.

The system also allowed the characterization of the smectic-A-hexatic-B transition in effectively two-dimensional two-layer thick free-standing films. These results provide a critical test of recent two-dimensional melting theory. The discrepancy between our data and the theoretical prediction suggests that our conception of the hexatic phase may not be complete.

E1.I02

FLUCTUATIONS IN FREELY SUSPENDED SMECTIC-A FILMS, <u>E. A. L. Mol</u>, A. N. Shalaginov, G.C.L Wong, and W. H. de Jeu, FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ, Amsterdam, The Netherlands

We report a quantitative experimental study of the displacement-displacement correlations in the thermal fluctuations of freely suspended smectic—A films. The measurements were performed by combining specular and diffuse x-ray reflectivity. The diffuse scattering probes the in-plane wave vector dependence of the fluctuations. This allows determination of the displacement-displacement correlation function and thus of the surface tension as well as the smectic bend and compression elastic constants. At long wavelengths the fluctuations are conformal, i.e. all layers fluctuate in unison, while at shorter length scales loss of conformality is expected. The fluctuations will be enhanced or quenched at the surface of the film, depending on whether the film has a fluorinated [1] or hydrogenated tail. Fluorination also has a profound effect on on the molecular formfactor as well as the in-plane length scales where conformality is lost.

[1] J.D. Shindler, E.A.L. Mol, A. Shalaginov, and W.H. de Jeu, Phys. Rev. Lett., 74, (1995), 722;

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E1.003

TEMPERATURE-INDUCED ORIENTATIONAL TRANSITIONS IN FREELY SUSPENDED NEMATIC FILMS, Andrei A. Sonin, Anand Yethiraj, <u>John Bechhoefer</u>, and Barbara J. Frisken, Dept. of Physics, Simon Fraser University, Burnaby BC V5A 1S6, Canada

We report observations of a temperature-induced orientational transition in a freely suspended nematic film of the liquid crystal 4-ethyl-2-fluoro-4'-[2-(trans-4-n-pentylcyclohexyl)-ethyl]-biphenyl (152). The transition is from a high-symmetry state where the molecules are perpendicular to the film boundaries (homeotropic alignment) to a lower-symmetry state where the molecules are inclined (tilted alignment) and occurs as the temperature of the sample is raised. A previous study by Faetti and Fronzoni (1978) discovered a similar transition in freely suspended nematic films of N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA), except that it occurred as the temperature was lowered, a result that we confirm here. In order to explain both orientational transitions and the temperature-independent alignment of other nematics, we have generalized a model by Parsons (1978) that is based on competition between polar and quadrupolar contributions to the surface free energy. By considering the effects of smectic ordering and ionic impurities, we can account for all of the various observations.

E1.004

NEMATIC BUBBLES IN FREELY SUSPENDED LIQUID CRYSTAL FILMS, <u>D. H. Van Winkle</u>, and F. Kettwig, Department of Physics and Martech, Florida State University, Tallahassee, FL 32306-3016, USA.

Nematic bubbles form in smectic freely suspended liquid crystal films when they are heated well above the bulk smectic to nematic transition temperature. In thin films, nematic droplets form and cause rapid film rupture. In some films, individual layers are seen to sweep off the surface, depending on the temperature, the thickness and the substrate. In thick films, these droplets occasionally remain stable for long periods. The shape of the droplets (in plane and perpendicular to the plane) allows determination of the local surface tension. A variety of dynamics are seen as a precursor to film rupture. Occasionally, isotropic regions are seen to form on these thick films before they rupture.

Supported by the Center for Materials Research and Technology.

E1.005

#### FERROELECTRICITY IN FREE-STANDING FILMS

<u>E.I. DEMIKHOV</u>, Institute of Solid State Physics, Rissian Academy of Sciences, 142432 Chernogolovka, Russia, University of Paderborn, Physical Chemistry, 33095 Paderborn, Germany

First theoretical results about ferroelectricity in 2D liquid-crystalline films have been published about 15 years ago by Pelcovits, Halperin Pikin, where a possibility of the true orientational long-range order in the 2D-SmC\* phase with high spontaneous polarization has been predicted. Experimental investigations of free-standing films have been limited until last time by achiral smectics and ferroelectric films with low spontaneous polarization. Recent progress in synthesis of materials with high P<sub>s</sub> enabled observations of qualitatively new properties. New periodical structure instabilities, resonance collective dynamics in the SmC\* phase and anomalous cross-over phenomena have been studied experimentally and theoretically [1]. It was shown that these phenomena essentially depend on the spontaneous polarization of the system. The periodical stripe texture of the SmC\* has been successfully explained as a new flexoelectric instability in an electric field produced by the films. All known properties of the resonance collective mode have been explained in the framework of the kink-switching concept. Properties of anti-, ferri- and ferroelectric phases are studied.

[1]. E.I. Demikhov and S.A. Pikin, JETP Lett. 61, 686, (1995); E.I. Demikhov, E. Hoffmann, S.A. Pikin et. al., Phys. Rev. E 51, 5954 (1995); E.I. Demikhov, S.A. Pikin and E.S. Pikin, Phys. Rev. E 52, 6250 (1995); E.I. Demikhov, JETP Lett. 61, 977 (1995).

## E1.006

SCALING OF BOND-ORIENTATIONAL ORDER PARAMETERS IN A 54COOBC TWO-DIMENSIONAL FILM, <u>C.F. Chou</u> and J.T. Ho, Department of Physics, State University of New York at Buffalo, NY 14260, USA, S.W. Hui, Department of Biophysics, Roswell Park Cancer Institute, Buffalo, NY 14263, USA, and V. Surandranath, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

Electron-diffraction measurements have been conducted on thin free-standing liquid-crystal films of n-pentyl-4'-n-pentanoyloxy-biphenyl-4-carboxylate (54COOBC). This compound undergoes the smectic-A-hexatic-B-crystal-B phase sequence, but its thin films exhibit power-law thermal anamolies at the smectic-A-hexatic-B transition which are not predicted in the theory of defected-mediated melting in two dimensions, despite the apparent absence of herringbone order. We have determined the 6n-fold bond-orientational order parameters  $C_{6n}$  in a two-layer film as a function of temperature in the hexatic-B phase. The results are consistent with the scaling relation  $C_{6n} = C_6^{o(n)}$ , where  $o(n) = n^2$ , as expected in a two-dimensional xy system.

E2.I01

TILTING CORRELATION IN ADJACENT LAYERS AND ORIGIN OF FERRO- AND ANTIFERRO-ELECTRICITY IN SMC\* -LIKE LIQUID CRYSTALS, Atsuo Fukuda, Tokyo Institute of Technology, Dept. of Organic & Polymeric Materials, Meguro-ku, Tokyo 152, Japan

Optical and spectroscopical studies have been performed. The chiral alkyl chain makes an angle >54.7° (the magic angle) with the core axis, precessing freely around it in Sm-A; the precession is biased toward the tilt-plane normal in Sm- $C^*$ . The carbonyl group near the chiral center rather lies on the tilt plane in antiferroelectric Sm- $C_A^*$ , while it takes a considerably upright position in ferroelectric Sm- $C^*$ . Consequently, in-layer spontaneous polarizations, emerging at smectic layer boundaries, are parallel and perpendicular to the tilt plane in Sm- $C_A^*$  and Sm- $C^*$ , respectively; the molecular rotational states as a whole determine ferro- and antiferro-electricity. When both of the states have nearly the same energies but are separated by a large barrier, the static Devil's staircase describable by the Bak-Bruinsma's Ising model emerges between Sm- $C_A^*$  and Sm- $C^*$ . As the barrier becomes smaller, the staircase acquires a dynamical character; when it almost diminishes so that any states between both of them are thermally excited equally, the non-correlated molecular tilting between adjacent layers realizes thresholdless antiferroelectricity. We have investigated these novel features by observing conoscopic figures and switching characteristics.

E2.I02

THRESHOLD PROPERTIES OF SSFLC IN TERMS OF POLARIZATION STRUCTURES, A. Mochizuki, T. Makino, H. Shiroto, Y. Kiyota and T. Yoshihara, Display Lab., FUJITSU LABS. LTD. 64 Nishiwaki, Ohkubo, Akashi 674 Japan

Bistability of the surface stabilized ferroelectric liquid crystal (SSFLC) is one of the most important factors of display performances. The electrooptic switching is based on the bistability which provides threshold characteristics to the SSFLC display device. Most of the electrooptic threshold properties of nematic devices are mainly decided by the surface anchoring at the interface between an alignment layer and liquid crystal molecules. The threshold properties of the SSFLC device which has a layer structure of liquid crystal molecules and provides an in-plane molecular switching are assumed to be governed by not only a surface anchoring but also a bulk structure itself. Here, We will show some experimental results which suggest contribution of liquid crystal bulk structure to the threshold properties. Layer structures: the bookshelf and the chyron geometries are one of the main bulk factors. The polarization structure depends on the layer structure. [1] The compressive and expansive environments to the SSFLC device lead to modulation of liquid crystal bulk structures. [2] The modulated bulk structure results in the different threshold properties in an SSFLC device. We also mention the gray shade capability of the SSFLC device in terms of the interaction between the surface anchoring and the bulk structure.

[1] A. Mochizuki et. al.; Ferroelectrics, 113, 353 (1991); 122, 37 (1991), Mol. Cryst. Liq. Cryst. 243, 77 (1994).
[2] S. Krishna Prasad et. al.; Ferroelectrics, 121, 307 (1991); 147, 351 (1994).

## E2.003

MONOMER HETEROGENEITY AND SUBSEQUENT PHOTOPOLYMERIZATION OF POLYMER STABILIZED FERROELECTRIC LIQUID CRYSTALS, C. Allan Guymon, and Christopher N. Bowman, Department of Chemical Engineering, University of Colorado, Boulder, CO, 80309-0424, USA.

Considerable attention has recently been given to polymerizations performed in a liquid crystal matrix. Systems of particular interest include ferroelectric liquid crystals (FLCs) mechanically stabilized by a small amount of polymer network. This study examines the polymerization behavior and kinetics of various amorphous and liquid crystalline diacrylates at various temperatures and in different liquid crystal phases. To help understand these effects, the segregation of these monomers before polymerization is also explored. The polymerization rate for all of the diacrylates is considerably faster in the higher order phases. The rate then approaches that seen in solvent polymerizations as the temperature is increased and the order of the phase decreases. The reasons for this rate increase in ordered phases are not the same for each of the monomers. For certain diacrylates the increase is driven by a decrease in the termination rate whereas both the termination and propagation rates increase for other diacrylates. This behavior indicates that different monomers segregate in different regions of the liquid crystal. Using infra-red spectrometry and X-ray diffraction, this segregation is observed to be highly dependent on the chemical structure of the monomer species.

## E2.004

ALIGNMENT OF FERROELECTRIC LIQUID CRYSTALS IN POLYMER NETWORK
Ruipeng SUN, Weisong ZHAO, Qingbing WANG, Yanqing Tian, Ximin HUANG, and Tao YU
LCL, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, P.R.CHINA

The polymer network ferroelectric liquid crystal devices in which the polymer is doped as 2.0% were investigated. It is difficult to obtain a good alignment in the cells under the polymerizing condition without extra field. However, by operating direct (or alternating) electric field in the polymerizing process, the unidirectional alignment of ferroelectric liquid crystals in the cells may be got very well. The measuring results of cone angle, response time and polymer network micro-structure and the interaction between polymer network and FLCs will be discussed and presented.

[1]. R. A. M. Hikmet, H. M. J. Boots, and M. Michelsen, Liq. Cryst., 19, 65 (1995)

[2] G. Lester, H. Coles, A. Murayama, and M. Ishikawa, Ferroelectrics, 148, 389 (1993)

#### E2.O05

FIELD-INDUCED INSTABILITIES IN CHIRAL SMECTIC LC SUPPRESSED BY A POLYMERIC NETWORK, M. Mitov<sup>(1)\*</sup>, H. Ishii<sup>(1)</sup>, S.T. Lagerwall<sup>(1)</sup>, P. Sixou<sup>(2)</sup>, G. Andersson<sup>(1)</sup> and L. Komitov<sup>(1)</sup>

<sup>1</sup>Chalmers University of Technology, Department of Physics, S-412 96 GÖTEBORG, Sweden.

<sup>2</sup>Laboratoire de Physique de la Matière Condensée (UA CNRS 190), Parc Valrose, F-06108 NICE Cedex 2, France.

\* Now at: CEMES-LOE (UPR CNRS 8011), BP 4347, F-31055 TOULOUSE, France.

Field-induced rotational instabilities may occur in chiral smectic liquid crystals subjected to an alternating electric field with an asymmetric addressing wave form [1, 2]. The initial smectic layer alignment becomes disordered and finally transforms into a chaotic structure. It is shown that these disturbances can be prevented by the UV polymerization of a few percents of cholesteric photo-crosslinkable material dispersed in the smectic liquid crystal. Polymerization was performed in samples in the A\* phase, C\* phase and isotropic phase. The influence of the polymeric network on the FLC material's electrooptic properties is investigated (tilt of the optic axis, response time, polarization). In addition to stabilizing the smectic layer order, the upper temperature stability of the liquid crystalline order is considerably raised, like a memory effect due to the network.

[1] G. Andersson, I. Dahl, L. Komitov, S.T. Lagerwall, M. Matuszczyk and K. Skarp, 13th ILCC, Vancouver, 1990.

[2] G. Andersson, T. Carlsson, S.T. Lagerwall, M. Matuszczyk and T. Matuszczyk, 4th FLC Conference, Tokyo, 1993.

**E2.006** 

ALIGNED FERROELECTRIC LIQUID CRYSTAL/POLYMER NETWORK DEVICES, W.J. Zheng, J. Hajto, <u>G H W Milburn</u>, Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh EH10 5DT, UK

We report here the preparation of fast switching ferroelectric liquid crystal/polymer network systems for display devices. A composite mixture was prepared using a dye doped ferroelectric liquid crystal mixture together with a UV curable adhesive. There is no requirement for special surface treatment of the cell substrate. The alignment of the composite film was achieved using an external magnetic field. Liquid crystal molecules were forced to orient parallel to the direction of the external field, and consequently, a particular configuration was obtained in the composite mixture. After UV curing of the material, the configuration was sustained, and a planar aligned composite layer was obtained. The aligned composite film has good electro-optic properties and possesses bistable switching.

#### E3.I01

NMR IN LIQUID CRYSTALS SPINNING AT AND NEAR MAGIC ANGLE, K.V. Ramanathan and C.L. Khetrapal, Sophisticated Instruments Facility, Indian Institute of Science, Bangalore 560 012, India

NMR spectra of liquid crystalline phases and the molecules dissolved therein, spinning at and near the Magic Angle provide information on the director dynamics and the order parameter.

The spectra near the critical concentration and temperature in mixtures of liquid crystals with opposite diamagnetic anisotropies show the switch over of the director orientation from the one with its preferential alignment along the axis of rotation to that perpendicular to it as a function of the spinning speed near the Magic Angle.

The spectra under slow spinning speeds exhibit a centre band and the side bands at integral values of the spinning speeds. The intensities of the spinning side bands contain information on the sign and the magnitude of the order parameter(s).

Such results are valuable particularly in the study of dynamic properties of the fatty acid chains in biological membranes and model systems.

Results obtained from such studies will be discussed with illustrative examples.

### E3.I02

# ORIENTATION, STRUCTURE AND DYNAMICS IN HIGHLY ORDERED SMECTIC PHASES BY <sup>2</sup>H NMR, L.Calucci, D.Catalano, C.Forte and C.A.Veracini

2H NMR is employed to study the behaviour of two partially deuterated mesogens: (I) 4'-hexyloxybenziliden-4-fluoroaniline[1] and (II) 4-(2'-methylbutyl)phenyl-4'-n-heptylbiphenyl-4-carboxylate [2]. Both I and II show nematic, smectic A and smectic B phases; II exhibits in addition a lower temperature smectic G phase. Measurements of orientational order for both I and II, as evaluated from the deuterium quadrupolar splittings, suggest that on entering the highly oriented smectic phases (B for I and B and G for II) the internal motions of the first two methylene groups in the chain slow down sensibly. The deuterium spin-lattice (T<sub>1Z</sub>) and quadrupolar (T<sub>1Q</sub>) relaxation times have been measured using a broadband multipulse Jeener-Broekaert sequence. The data are discussed on the basis of rotational diffusion theories, internal motions and collective order fluctuations.

C.Forte, C.Gandolfo, M.Geppi and C.A. Veracini, Mol. Cryst. Liq. Cryst. 266, 213 (1995)
 K.Fodor-Csorba, L.Bata, S.Holly, E.Gács-Baitz and K. Ujszászy, Liq. Cryst. 14, 1863 (1993)

E3.003

DYNAMIC MECHANICAL AND 14N-NMR STUDIES ON STRUCTURE OF D-PHASE

Masataka Tansho, Takanori Yamaguchi<sup>†</sup>, Shoichi Kutsumizu<sup>††</sup> and Shinichi Yano<sup>††</sup>

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaragi 305, Japan. †Tsukuba Research Lab. Sumitomo Chemical Co. Ltd., 6 Kitahara, Tsukuba, Ibaragi 300-32, Japan. ††Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan.

4'-n-Alkoxy-3'-nitrobiphenyl-4-carboxylic acids (ANBC-n, n: cabon of no. of n-alkyl) show D-phase, an optically isotropic mesophase, in the high homologues (n≥15). To date, a lot of X-ray studies have been done for D-phase of ANBC, and several structural models have been proposed. The present work is undertaken to disclose the structure of the D-phase by dynamic mechanical and <sup>14</sup>N-NMR spectral studies. From the dynamic mechanical measurements, it was found that the storage modulus is an extraordinary high value of 10<sup>7</sup> dyne/cm<sup>2</sup> in the D-phase, compared with 10<sup>3</sup>-10<sup>4</sup> dyne/cm<sup>2</sup> in smectic A and C phases. On the other hand, <sup>14</sup>N-NMR spectra showed that the D-phase is isotropic and undergoes two rate processes for the molecular motions, faster and slower motions. At the conference, we report that these results support the interpenetrating jointed rod (IPJR) model that the D-phase consists of 3-d network structure jointed by rod-like micelles.

E3.004

DETECTION OF SECOND-ORDER DIRECTOR FLUCTUATIONS BY DEUTERON SPIN-SPIN RELAXATION AT A STANDARD HIGH FIELD, Ronald Y. Dong, Department of Physics and Astronomy, Brandon University, Brandon, Manitoba, Canada R7A 6A9.

We report on the measurement of deuteron spin-spin relaxation time  $T_2$  in the nematic phases of p-methoxy-d<sub>3</sub>-benzylidene-d<sub>1</sub>-p-n-butyl-d<sub>9</sub>-aniline and 4-n-pentyl-d<sub>11</sub>-4'-cyanobiphenyl-d<sub>4</sub> using the quadrupolar echo pulse train,  $90_x$ - $\tau$ - $90_y$ - $(2\tau$ - $90_y)_n$ , in a magnetic field of 7T. The zero frequency spectral densities  $J_0(0)$  at different carbon sites are derived from the  $T_2$  measurements. While the spectral densities  $J_1(\omega_0)$  and  $J_2(2\omega_0)$ , where  $\omega_0/2\pi=46$  MHs, could be interpreted using a model [1] that is based on the rotational diffusion motion of individual molecules and internal bond rotations in the end chain, the measured  $J_0(0)$  appears to be too large. It is argued that second-order director fluctuations [2] are the additional relaxation mechanism needed to interpret the  $J_0(0)$  spectral densities. We believe that experimental  $T_2$  data at a high magnetic field could be used under favourable conditions to gain insights on director fluctuations.

- [1] R.Y. Dong, "Nuclear Magnetic Resonance of Liquid Crystals", Springer-Verlag, New York (1994).
- [2] R.L. Vold, R.R. Vold, and M. Warner, J. Chem. Soc. Faraday Trans. II 84 97 (1988).

E3.005

VIBRATIONAL PROPERTIES OF LIQUID CRYSTAL MOLECULES, S. J. Clark, C. J. Adam and J. Crain, Department of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3JZ, UK.

We determine the molecular vibrational frequencies and displacement patterns for the 4-4' pentyl-cyanobiphenyl (5CB) molecule by first principles density functional theory. These dynamic properties are obtained directly by diagonalisation of the dynamical matrix, the elements of which are determined from quantum mechanical Hellmann-Feynman Forces. Periodic boundary conditions are used which allow for expansion of the molecular electronic wavefunction in terms of a delocalized plane wave basis set. The advantage of this approach is that no basis-set-related corrections enter the evaluation of forces. These calculations are in excellent agreement with the results of vibrational spectroscopy and they provide a reliable means of predictive modelling of molecular properties and can be applied to as yet unsynthesised molecules.

## E3.006

SHAPE DOMINATED ORDERING IN NEMATIC SOLVENTS. A DEUTERIUM NMR STUDY OF CYCLOALKANE SOLUTES\*, A.F. Terzis\*, D. J. Photinos\*, C.-D. Poon\*, E. T. Samulski\*, Z. Luz\*, R. Poupko\*, H. Zimmermann\*, K. Muller\*, and H. Toriumi\*, \*Department of Physics, University of Patras, Patras, Greece 26110, \*Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA, \*Weizmann Institute of Science, Rehovot, Israel 76100, \*Department of Chemistry, University of Tokyo, Komaba, Tokyo 153, Japan.

We analyse the NMR spectra of a series of deuteriated cyclic aliplatic solutes in a nematic solvent, and demonstrate that their orientational ordering can be accurately described in terms of purely excluded volume interactions with the solvent molecules. These interactions are treated explicitly in the context of a statistical mechanical approximation[1] wherein the orientational correlations among the solvent molecules are not taken into account directly. We test the theory by predicting the observed order parameters of the aliphatic solutes as determined with deuterium NMR. The utility and limitations of a description of solute ordering exclusively from hard-body interaction is discussed.

[1] A.F. Terzis, and D.J. Photinos, Mol. Phys., 83, 847 (1994).

<sup>\*</sup> Work suported by the NSF Grant DMR-9412701.

### FREE ENERGY AND THE ORDER PARAMETERS OF STOCKMAYER FLUIDS.

K. Szumilin<sup>†</sup> and J.J. Milczarek<sup>‡, †</sup>Institute of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland, <sup>‡</sup>Institute of Atomic Energy, 05-400 Otwock, Poland

The system of spherical particles with embedded electrical dipoles (Stockmayer fluid) [1] has been considered. The interaction potential consists of the hard core and the long-range dipole-dipole components. The free energy of the system was calculated in terms of the expansion coefficients of the single-particle distribution function in generalized Fourier series [2]. The critical temperature was determined for each coefficient of this expansion. The order parameters have been selected from the expansion coefficients with maximal critical temperature. It is shown that the critical temperatures and order parameters depend on the size and shape of the system.

[1] B. Groh and S. Dietrich, Phys. Rev. E50, 3814 (1994)

[2] K. Szumilin and J.J. Milczarek, Liquid Crystals, 14, 1033 (1993)

A1P.02

THE EFFECT OF A RIGID AND NON-POLAR SOLUTE ON ELASTIC CONSTANTS OF 8CB, P.CHATTOPADHYAY, S.K.ROY, DEPT.OF PHYS, JADAVPUR UNIVERSITY, CALCUTTA-700 032, W.B., INDIA.

Guo etal. [1] have investigated the effect of solutes like hexane, benzene etc. on the ordering of the liquid crystalline solvents 7CB and 8CB. They observed that the incorporation of hexane in 8CB reduces  $T_{NI}$  more significantly than  $T_{SN}$ . They also remarked that the solute molecules do not have appreciable preferential association with any special part of the solvent molecule. We have investigated the effect of mixing the non-polar solute biphenyl in 8CB and have measured  $\Delta\epsilon$ ,  $K_{11}$  and  $K_{33}/K_{11}$  for five different concentrations. The experiment consisted of the measurement of capacitance using a HP4194A LCR meter [2]. The change in both  $T_{NI}$  and  $T_{SN}$  with concentration were also measured using the Mettler Hot Stage ranging 30°C to 38°C. We find that  $T_{SN}$  changes more significantly than  $T_{NI}$ . The  $\Delta\epsilon$  and the  $K_{11}$  were found to decrease with increasing concentration of the solute while  $K_{33}/K_{11}$  increases as a result of adding the solute.

[1] W.Guo, B.M.Fung, Liq.Cryst., 9, 117-126, (1991);[2] P.Chattopadhyay, S.K.Roy, Mol. Cryst. Liq. Cryst., 257, 89-98, (1994)

A1P.03

DYNAMIC LIGHT SCATTERING FROM A DISK-LIKE THERMOTROPIC NEMATIC PHASE (ND), T. Othman. N. Derbel, A. Gharbi, Laboratoire de Physique des Cristaux Liquides et des Polymères, Faculté des Sciences de Tunis - Campus Universitaire - 1060 Le Belvédère - Tunisie.

We have measured separetely the orientational diffusivities  $D_{splay}$ ,  $D_{twist}$  and  $D_{bend}$  corresponding respectively to splay, twist and bend deformations. The material used is the "hexa-n-alkanoyloxytruxene" (HATX  $C_{12}$   $H_{25}$ ).  $D_{splay}$ ,  $D_{twist}$  and  $D_{bend}$  are about 100 times weaker than those corresponding to rod-like thermotropic nematic[1]. They present the same ratios as for rod-like nematic phase although there is a difference between the geometrical shape of the two kinds of molecules. This result can be explained by the appearance of a local order of thermotropic nematic type. This order occurs in the packing of a few molecules to form relatively short columns of diameter of individual disk. So, deduced numerical values of elastic constants ( $K_{11} \approx 0.45.10^{-6}$  c.g.s.,  $K_{22} \approx 1.1.10^{-6}$  c.g.s.,  $K_{33} \approx 0.22.10^{-6}$ c.g.s.) shows that  $K_{11} > K_{33}$  for discotic whereas  $K_{33} > K_{11}$  for rod-like molecules. For disk-like molecules,  $K_{22}$  is the largest elastic constant, while for rod-like molecules, it is the smallest one. The backflow effects are more important on the bend distorsion than on splay one, since  $\eta_{twist}/\eta_{splay} \approx 3$ .

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BIDISPERSE LIQUID CRYSTALS PHASE BEHAVIOUR OF A MIXTURE OF GENER-ALISED GAY-BERNE RODS, R.A. Bemrose\*†, C.M. Care†, D.J. Cleaver† and M.P. Neal‡, † Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield, S1 1WB, UK and ‡ Department of Mathematics and Computing, University of Derby, Kedleston Road, DE22 1GB, UK

We present results for the phase behaviour of a bidisperse liquid crystal mixture from two molecular dynamics investigations within the isobaric-isothermal (NPT) ensemble using the generalised Gay-Berne potential [1]. Firstly, to clarify the effect of length dispersity, the length to breadth ratios of molecular species 'A' and 'B' were chosen as 3.5:1 and 3:1 respectively. Temperature sweeps at a range of pressures  $1 \le \langle P^* \rangle \le 5$  of a 50% mixture identified nematic and isotropic-smectic co-existence regions similar to those observed for one component Gay-Berne systems [2]. Also, variations of the molecular concentrations has revealed an extended nematic phase and the postponement of the smectic phase. Secondly, we have studied the possibility of liquid crystal formation from simulations of mixtures of non-mesogenic molecules by using species with length to breadth ratios of 2:1 and 5:1 respectively.

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- \*Supported by EPSRC bursary and DRA Case award

## A1P.05

#### ORIENTATIONAL ORDER IN LIQUID CRYSTALS LAYER

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We used the Gay-Berne potential [1,2] and computer simulation to study anisotropic molecules in 2D. In order to present a thin liquid crystals layer between two plates, the molecules were restricted by two boundaries along one axis, while in other direction periodic boundary conditions were applied. The nearest image convention and cut-off were applied to improve the performance of the Monte Carlo method [3,4]. The influence of anchored molecules, density and temperature on orientation inside the layer was observed.

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#### A1P.06

PROPERTIES OF AN IDEAL NEMATIC GAY-BERNE FLUID, Wilfried L. Wagner, Institut für Theoretische Physik, Technische Universität Berlin, Sekr. PN 7-1, D-10623 Berlin, Germany

We have investigated the thermodynamical and structural properties of a fluid of perfectly oriented Gay-Berne particles. Following the proposal of Lebowitz and Perram [1] an affine mapping was applied to transform the properties of a system of parallel hard ellipsoids of revolution to those of hard spheres. The connection between hard-core particles and soft-core particles was established by generalization of the blip-function theory [2] to anisotropic potentials. For a given axial ratio c/a of the hard ellipsoid the axes c and a were used as adjustable parameters in the perturbation scheme. The pressure versus density was determined for different temperatures and compared with the simulation results of de Miguel et al. [3]. We have analysed the longitudinal and transversal components of the pair correlation function. They do not become identically by an appropriate scaling of the contact distance. We have also investigated the influence of different axial ratios  $\sigma_2/\sigma_1$  and well depths of the Gay-Berne potential on the thermodynamical results.

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#### REAL AND COMPUTER EXPERIMENTS ON NEMATIC LIQUID CRYSTALS,

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The nematic phase formed by 4-n-pentyl-4'-cyanobiphenyl (5CB) was investigated using molecular dynamics (MD) simulation and NMR spectroscopy. Both neat 5CB liquid crystal [1] and a nematic mixture of 5CB and benzene [2] were studied. The computer simulations were performed using realistic atom-atom potentials for both solvent and solute molecules. Distributions of torsional angles and relative populations of the conformations in the alkyl chain were determined. The molecular organisation was investigated by calculating order parameters and orientational distribution functions. Average intermolecular interaction parameters were evaluated from the distribution functions using simple mean field theory (MFT). The interaction parameters were compared with the results from an MFT analysis of order parameters determined from NMR spectroscopy. The validity of several approximations made in the MFT were tested in the computer simulation. Translational and reorientational molecular motions were investigated by calculating relevant time correlation functions.

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A1P.08

LARGE-SCALE SIMULATION STUDIES OF CYANOBIPHENYLS\*, <u>Yves Lansac</u>, Matthew A. Glaser, and Noel A. Clark, Department of Physics, University of Colorado, Boulder, CO, 80309, USA.

Cyanobiphenyls (nCBs) represent a useful and intensively studied class of mesogens. Many of the peculiar properties of nCBs (e.g. their anomolously low dielectric anisotropy relative to Debye model predictions and the partial bilayer character of the Smectic  $A_d$  phase) are thought to be a manifestation of short-range antiparallel association of neighboring molecules, resulting from strong dipole-dipole interactions between cyano groups. To test and extend existing models of microscopic ordering in nCBs, we have carried out a series of large-scale molecular dynamics simulations of 5CB and 8CB in the Isotropic, Nematic, and (for 8CB) Smectic  $A_d$  phases, and have measured a wide variety of thermodynamic, structural, and dynamical properties of these materials. Specific comparisons of our results with experimental measurements were made in order to validate our molecular model and interaction potential. We have also initiated exploratory studies probing the influence of specific electrostatic interactions and of molecular flexibility on the properties of nCBs.

\*Work supported by NSF Materials Research Group Grant DMR 92-24168.

A1P.09

A STATISTICAL THEORY OF VISCOSITY OF NEMATIC LIQUID CRYSTALS, G.S. Bo-kun, V.S. Vikhrenko, A.V. Kondratenko, and <u>V.B. Nemtsov</u>, Belarussian State Technological University, 13a, Sverdlova Str., Minsk, 220 630, Belarus.

The general methods of the nonequilibrium statistical thermodynamics are used to describe the viscosity of nematic liquid crystals. The expressions for the viscosity coefficients in terms of time correlation functions are given and in this way the method of calculation and prediction of the coefficients from the first principles is proposed. The time correlation functions are evaluated on the basis of kinetic equations. The rotational friction coefficients involved in this equation are considered as calculated quantities. The final formulae relate the viscosity coefficients to the number particle density, the order parameter and the molecular parameters. These expressions give the explicit connection between the shape and size parameters of molecules and hydrodynamics of media composed of such molecules. Calculations by the formulae satisfactorily agree with the experimental data on the viscosity coefficients for a number of nematics.

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SPATIAL MODEL OF LIQUID CRYSTAL ANISOTROPIC PROPERTIES IN HEAT FIELDS, George L. Nekrasov, Institute of Electronics, Byelarus Academy of Sciences, 22, Logoiski Tract, Minsk, 220090, Byelarus

Simple computation method of total ellipsoid family for mutual connection definition between fundamental anisotropic characteristics, such as refraction indexies, dielectric constants, absorption coefficients, effective molecular polarizabilities, et. al. has been proposed.

Calculation methods make possible to obtain all the data by measuring only one parameter in isotropic phase. Obtained relationships have been tested on many experimental data of other authors and they are some different from model local field relationships of Lorents-Lorents, Neugebauer, Vuks.

Estimation opportunity of external action inducted anisotropic molecules is discussed.

## A1P.12

A STUDY OF NEMATOGENIC BEHAVIOUR OF LIQUID CRYSTALS, <u>D. P. Oiha</u>, D. Kumar & M. Roychoudhury, Department of Physics, University of Gorakhpur, Gorakhpur (U. P.) 273 009, INDIA.

configuration made to determine the attempt been preference of a pair of nematic liquid crystal molecule, PMBAMC, and motions. with respect to translatory rotational modified Configurational energy hee been computed ueing Rayleigh-Schödinger perturbation method and corresponding probabilities have been calculated using MB statistics. to identify the most probable attempt been made configuration at phase transition temperature and to explain the nematogenic behaviour of these liquid crystals and thereby develop a molecular model for the liquid crystallinity.

# A1P.13

THEORETICAL STUDY ON SOME THERMOTROPIC LIQUID CRYSTALS, Nitish K. Sanyal & S. N. Tiwari, Department of Physics, University of Gorakhpur, Gorakhpur (U. P.) 278 009, INDIA.

crystalline behaviour of some thermotropics anisaldehyde azine, p-azoxyanisole, 4'-methoxy benzylidene acetoxy aniline, ethyl p- azoxybenzoate etc. has been studied. Modified Rayleigh-Schrödinger perturbation treatment has been used to evaluate intermolecular interactions. Both in-plane and stacking interactions between a pair of liquid crystal molecules have been considered. Molecular charge distribution and other physico- chemical parameters have been computed using CNDO/2 method. Further, the probability of occurrence of molecular complexes at phase transition has been analysed using MB statistics. Attempts have been made to develop a model to characterize mesogenic behaviour of thermotropic liquid crystals.



#### MOLECULAR DYNAMICS SIMULATIONS OF LIQUID CRYSTALS,

Sten Sarman, Department of Physical Chemistry, Göteborg University, S-412 96 Göteborg, SWEDEN

We have applied a molecular dynamics algorithm that makes the director angular velocity a constant of motion. Setting this velocity equal to zero means that a director based coordinate system becomes an inertial frame. This is a great advantage because most properties of liquid crystals are best expressed relative such a coordinate system. One also prevents the director reorientation from interfering with the tails of slowly decaying time correlation functions. The algorithm is very useful when it is combined with various nonequilibrium molecular dynamics methods. This greatly facilitates the study of shear flow and the evaluation of transport coefficients such as diffusion coefficients, thermal conductivities and viscosities. We have used the director constraint algorithm to examine various transport properties of liquid crystal phases of the Gay-Berne fluid.

A1P.15

CONFORMATION ENERGY SURFACE FOR LIQUID CRYSTAL MOLECULES FROM FIRST PRINCIPLES CALCULATION: APPLICATION TO 5CB, S. J. Clark, C. J. Adam and J. Crain, Department of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3JZ, UK.

We have performed first principles molecular dynamics calculations to investigate the structure and conformation of the liquid crystal molecule 5CB which contains a pentane chain joined to two phenyl rings terminated by a cyanide group. We describe the electronic structure by using density functional theory within the generalized gradient approximation for electron exchange and correlation and expand the electronic wavefunctions in a plane wave basis set. Structural optimization of atomic positions is performed to obtain the relaxed molecular geometry. The relative angle between the two phenyl rings and the angle of the pentane tail is allowed to vary. For each possible pair of angles we calculate the total energy of the structure from which we obtain the energy surface for these conformations. We find the optimum conformation of the molecule is non-planar with a relative angle between the phenyl rings of 31°, in excellent agreement with recent NMR data. The angle of the pentane tail has a small, but significant effect on the energetics of the molecule. From this energy surface we fit an accurate intramolecular potential to be used in large empirical simulations of liquid crystals.

A1P.16

COMPOSED OF HYPOTHETICAL DIATOMIC MOLECULES, K.Sunohara, T.Narui, K.Asaba and S.Kobinata, Department of Materials Science and Technology, Toin University of Yokohama, 1614 Kurogane-cho, Midori-ku, Yokohama, 227, JAPAN

Computer simulations (Monte Carlo and molecular dynamics) were carried out for the system composed of hypothetical diatomic molecules. Intermolecular potentials were calculated as the sum of the (6,12) type Lenard-Jones site-site potentials. By changing the Lenard-Jones parameters ( $\sigma$  and  $\epsilon$ ) for a fixed bond length, we can make virtual diatomic molecules of various shapes. For the system composed of such virtual diatomic molecules, temperature and pressure dependence of various physical quantities (order parameter  $\langle P_2 \rangle$ , internal energy,...) were studied in detail. For the assembly of some elongated diatomic molecules, liquid crystalline state were found to appear. Detailed inspection shows the predominant importance of molecular shape or repulsive part of intermolecular interaction for the appearance of liquid crystalline state.



A THEORETICAL STUDY OF VARIATION OF ENTROPY WITH RESPECT TO MOLECULAR VOLUME IN NEMATIC LIQUID CRYSTAL, M. Roychoudhury & D. Kumar, Department of Physics, University of Gorakhpur, Gorakhpur (U. P.) 273 009, INDIA.

Estimation of change in entropy with respect to molecular volume been carried out under Maxwell Boltzmann statistical frame nematic liquid crystals at work. Studies have been taken up for has been calculated from constant temperature. Molecular volume calculation Entropy separation. intermolecular volume. ALL epecific molecular at. probability configurational geometrical inputs been performed using the computations have optimization and literature. Structural crystallographic from out peremeters of molecular calculation through quatum mechanical methods.

## A1P.18

MOLECULAR DYNAMICS SIMULATIONS OF LIQUID CRYSTAL PHASE TRAN-SITIONS, Keiko M. Aoki and Tetsuo Akiyama, Department of Chemical Engineering and Materials Science, Shizuoka University, 3-5-1 Johoku, Hamamatsu 432, Japan

Phase transitions in a sequence of crystal-smectic-nematic-isotropic states are investigated by constant pressure molecular-dynamics (MD) simulations, in which the hydrostatic pressure is preserved [1]. The MD simulation uses a simple model representing soft spherocylinders having both translational and orientational freedoms [2]. This model enables us to investigate to what extent can the properties known to real liquid crystal phases be explained by the anisotropy of the molecular shape alone. We observe, through the simulation, not only the macroscopic properties at the transition, such as volume change, but also the microscopic properties as well. Anisotropic diffusion of the molecules in liquid crystal phases is also investigated.

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# A1P.19

COMPUTER SIMULATION OF ROTATOR PHASES IN LIQUID-CRYSTALLINE POLYMERS, T.L.Phillips, Z.A. Saigol and S. Hanna, Physics Dept, Bristol University, Tyndall Avenue, Bristol, BS8 1TL, UK.

Polymeric rotator phases are mesophases in which the polymer chains are arranged on a 2-dimensional lattice, but possess some degree of dynamic rotational disorder about the chain axis. They are usually referred to as either highly ordered smectic liquid crystals, columnar phases or plastic crystals. Rotator phases are particularly common in mainchain liquid crystal polymers, although they are not restricted to this class of material, and are now thought to play an important role in the crystallisation of polyethylene. The aim of the current work is to explore the high temperature behaviour of poly(hydroxybenzoic acid) (PHBA). PHBA is a crystalline polymer which forms an important component of several commercial liquid-crystalline polymers. It undergoes a first order phase transition to form a pseudohexagonal rotator phase, at 340°C. Although several attempts have been made to establish the nature of this rotator phase, its structure is, as yet, poorly understood. We have performed Monte Carlo simulations on idealised rotator phase models, using energy terms and cell parameters derived from PHBA. By this means we have been able to reproduce the crystal-rotator phase transition, as well as generating diffraction patterns which agree qualitatively with experimental X-ray and electron diffraction data. We will discuss the structural changes which occur in the rotator phase, as the temperature is increased, and compare our results with previous models which were derived from diffraction data on the basis of symmetry arguments.

MOLECULAR ORDERING AND EVEN ODD EFFECT IN HOMOLOGOUS SERIES OF p-n-ALKOXYBENZOIG ACIDS: A QUANTUM MECHANICAL STUDY, M. Rovchoudhury and D. Kumar, Department of Physics, University of Gorakhpur, Gorakhpur (U. P.) 273 000, INDIA.

A theoretical analysis has been carried out to determine the intermolecular association energy of 10 homologues of p-n-alkoxy benzoic acid series. Configurational energy has been computed using modified Rayleigh-Schödinger perturbation method. Molecular charge distribution and dipole moments etc. have been evaluated using all valence quantum mechanical method. Configurational geometry has been optimized using self developed computer program. A comparative picture of association energy vs homologue number will be presented in the light of even odd effect.

A1P.21

PROBE TWISTING POWER AND ORDERING: THE ROLE OF MOLECULAR SHAPE A. Ferrarini and P.L. Nordio\*, Department of Physical Chemistry, University of Padova, Italy.

A shape model is used to predict the ordering properties of molecular dopants inducing chiral mesophases. Two tensorial properties associated to the molecular morphology are defined: a surface tensor, which determines the alignment of the molecular axes, and a helicity tensor which accounts for the chiral features of the probe. Solute ordering matrix and helical twisting power, i.e. magnitude and handedness of the pitch in the induced cholesteric phase, are then calculated as functions of temperature in terms of solvent properties such as strength of potential of mean torque and twist elastic constant. The excellent agreement between model predictions and the experimental data reported for various classes of chiral solutes provides evidence for the important role played by molecular shape. The effects of chemical substitution and conformational dynamics are analysed, and extension of the model to chiral Smectic-C\* mesophases is discussed.

A. Ferrarini, G.J. Moro, and P.L. Nordio, Liq. Crystals 19, 397 (1995); Phys. Rev. E 53, 681 (1996). \* Human Capital and Mobility Network Project N. 930282.

A1P.22

MULTIPLE LIGHT SCATTERING IN NEMATIC LIQUID CRYSTALS, Holger Stark, Tom Lubensky, Kristen Jester, Ming Kao, and Arjun Yodh, Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, USA.

In nematic liquid crystals light is strongly scattered from director fluctuations. We are interested in the limit where the incoming light wave is scattered many times. Then, the light transport can be described by a diffusion equation for the light energy density with diffusion constants  $D_{\parallel}$  and  $D_{\perp}$ , respectively, parallel and perpendicular to the director. Extending the theory for isotropic systems we have developed a method to calculate these diffusion constants. We discuss how  $D_{\parallel}$  and  $D_{\perp}$  depend on the Frank elastic constants, the dielectric anisotropy, and an applied magnetic field and compare our theoretical predictions with experiment. Temporal correlations of the diffusing light probe the dynamics of director modes on much shorter time scales than single light scattering experiments. To account for the decaying temporal correlations, one has to add an absorption term to the diffusion equation, which we also discuss. Finally, we comment on coherent backscattering in nematic phases.



MOLECULAR DYNAMICS SIMULATION OF SURFACE ANCHORING EFFECTS ON LIQUID CRYSTAL ORIENTATION, Masafumi Yoshida and Hirokazu Toriumi\*, Department of Chemistry, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan (\*corresponding author)

Molecular dynamics (MD) simulation was carried out for a model liquid crystalline system to understand the effect of surface anchoring on the molecular orientation in liquid crystals. The model system is composed of "beads model molecules" (linearly connected Lennard-Jones particles) placed between two twisted model alignment layers. The Lennard-Jones type potential used here takes care of both attractive and repulsive interactions between segmental interaction elements, and can easily be expanded to include the Coulombic interactions, the shape effect, and other structure factors. The orientational distribution calculated as a function of the distance from the surface can visualize the effect of surface anchoring on the spatial distribution of liquid crystalline molecules. The effect of surface anchoring is more clearly illustrated when the dynamics of the field-induced reorientational transition is analyzed in a twisted nematic cell that involves both twist and bent deformation modes.

## A1P.24

TOPOLOGICAL DEFECTS IN A NEMATIC FILLED WITH COLLOID PARTICLES, O.V. Kuksenok<sup>(a)</sup>, R.W. Ruhwandl<sup>(b)</sup>, S.V. Shiyanovskii<sup>(a)</sup>, E.M. Terentjev<sup>(b)</sup>

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b) Cavendish Laboratory, University of Cambridge, CB3 0HE, UK.

We theoretically investigate topological constraints and the defect structure around a spherical body immersed in a uniform nematic liquid crystal. Depending on the strength of anchoring on the particle surface, there are three possibilities. At rigid anchoring, WR/K >> 1, the inner surface constraint forces a disclination ring of a radius  $a \propto 1.25 * R$ , with R the particle size. At a lower, critical value  $W^* (W^* \propto (a^3/R^4)K \approx 2K/R)$  the disclination rings contracts to the surface and, for small anchoring, WR/K << 1, the director distribution is regular, defect-free. We obtain a full numerical solution of the problem and also a compact analytical expression for  $\mathbf{n}(\mathbf{r})$ , which has a characteristic asymptotic behaviour  $\delta \mathbf{n} \propto r^{-3}$  at large distances. This leads to a specific anisotropic long-range interaction between such colloid particles in a nematic matrix.

# A1P.25

ON THE DIFFERENT BEHAVIOUR OF SIMPLE LIQUIDS AND LIQUID CRYSTALS IN CA-PILLARY RISE EXPERIMENTS, Christina Papenfuss and Wolgang Muschik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

The balance equations for surface densities in two dimensional liquid crystals are presented. In order to get a closed system of differential equations constitutive equations are needed. These constitutive equations are restricted by the Second Law of Thermodynamics. From these restrictions the surface stress tensor is calculated. It is shown that the normal stresses do not vanish. They have an influence in capillary rise experiments for measuring the surface tension: For simple liquids the easiest way to measure the surface tension is the determination of the height of the liquid in a capillary and the contact angle of the liquid at the glass surface. In the case of simple liquids there is an algebraic relation between these quantities and surface tension. This is not the case for liquid crystals. There one has a differential equation relating surface tension to the measured quantities. This results in an influence of boundary conditions.

COMPUTER SIMULATION STUDY OF THE RAYLEIGH SCATTERING IN THE ISOTROPIC PHASE OF PCH5. <u>S.Ye, Yakovenko</u>, A.A.Muravski, F.Eikelschulte and A.Geiger, Institute of Applied Physics Problems, Kurchatova 7, Minsk, 220064, Belarus Dortmund University, Otto-Hahn-Strasse 6, D-44221 Dortmund, Germany.

Configurations of 200 p-n-pentyl-(p'-cyanophenyl)- cyclohexane (PCH5) molecules from molecular dynamics simulations were used to calculate the Rayleigh light scattering spectra of the isotropic phase. The interaction induced contribution is calculated to the first order dipole-induced dipole terms in the point molecular polarizability approximation. The effect of the size of the simulated system is checked from different points of view. Molecular flexibility is explicitly taken into account and comparisons in terms of time correlation functions are performed. Studies of the different contributions induced by the isotropic and the anisotropic part of the molecular polarizability, evidenced the negligibility of the second one and showed the importance of orientational-translational intermolecular correlations for spectra formation in mesogen systems.

A1P.27

NOVEL BIFURCATION SET CROSS-SECTION METHOD FOR TOPOLOGICAL ANALYSIS OF PHASE DIAGRAMS, V. A. Konoplev, A. V. Khomenko, and VI. K. Pershin\*, Theoretical Physics Department, Ural State Technical University, Ekaterinburg, 620002, RUSSIA.

A comprehensive theoretical investigation of complex models, in particular, liquid crystals is often difficult or even impossible because of the latters include more then 3-5 parameters (thermodynamical and material constants). In this connection two versions of bifurcation set cross-section method are proposed which allow to construct all the possible, at least two-dimensional, phase diagrams (PDs) of models under consideration. The bifurcation set (separatrix) of thermodynamic potential F is defined by conditions  $\nabla F(x,c)=0$ ,  $\det(\hat{\sigma}^2 F/\hat{\sigma}x,\hat{\sigma}x_j)=0$ , where  $\mathbf{x}=(\mathbf{x}_1,...,\mathbf{x}_k)$ - order parameters. The knowledge of separatrix surface in the "control parameters" ( $\mathbf{c}=(\mathbf{c}_1,...,\mathbf{c}_n)$ ) space permits to define stability boundaries of various phase states. As an example, the method is applied to the investigation of the thermodynamic potential of the  $\mathbf{X}_{1,0}$  type catastrophe for the description of smectic A mesophase and it is obtained 38 topologically different types of PDs. Among other results, the most important one is that all the critical (end critical, tri-critical etc.) points of PDs are peculiar points of the separatrix [1].

[1]. Vl.K.Pershin, Zurn.Fiz.Khim., **69**, 67 (1995). \*Supported by RFFI Grant No 95-02-04783

A1P.28

MOLECULAR DYNAMICS SIMULATIONS OF SURFACE-INDUCED ORDERING IN A NEMATIC LIQUID CRYSTAL<sup>†</sup>, <u>J. Stelzer</u>, P. Galatola\*, G. Barbero\*, and L. Longa, Instytut Fizyki, Uniwersytet Jagielloński, Kraków, Poland, \*Dipartimento di Fisica, Politecnico di Torino, Italy.

The changes in the structure of a uniaxial nematic liquid crystal in contact with an orienting surface have been investigated by means of molecular dynamics simulations. The bulk molecular interactions were modelled by the well-established Gay-Berne potential. The anisotropic surface was described by an anisotropic one-dimensional Lennard-Jones potential. In order to model a rough interface, we considered a surface whose height is sinusoidally modulated along the transversal directions (x, y). All simulations were performed in the nematic range of the Gay-Berne phase diagram. — The z-profile of the tensor order parameter Q and of the particle density have been calculated. In contact with the surface, two smectic C layers are induced. Moving towards the bulk, the smectic order disappears and a decrease of the uniaxial orientational order below its bulk value occurs. This intermediate region between the surface-induced smectic C ordering and the bulk nematic is characterized also by a considerable degree of biaxiality. Correspondingly, the director orientation undergoes a strong distortion close to the surface.

<sup>†</sup> Work supported by the EEC (contract no. ERBCHRXCT93019)



ELASTIC INTERACTION OF A SUSPENDED SOLID PARTICLE WITH AN INTERFACE IN A NEMATIC LIQUID CRYSTAL

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Yu. Raikher, Institute of Continuum Media Mechanics, Urals Branch of RAS, Perm, 614061, Russia

We study the force balance on a rod-like solid particle (non-Brownian) embedded in a nematic liquid crystal (NLC) in a neighbourhood of an interface (e.g., a wall) with planar or homeotropic boundary conditions for the NLC director on it. The solution of this problem is essential to understand the structure and properties of LC-suspensions of any kind; but in particular ù of ferroliquid crystals, i.e., suspensions of single-domain ferroparticles in ordinary NLC. In our model we replace the particle by a set of fictitious disclination lines positioned inside it. The arrangement of this disclination bundle is flexible that allows to fit the actual boundary conditions on both the particle surface and on the neighbouring wall. We describe the structure and energy of the system NLC + one particle and discuss the propereties of the resulting elastic force.

## A1P.30

A METHOD OF CALCULATION OF VISCOSITY COEFFICIENTS OF BIAXIAL NEMATIC LIQUID CRYSTALS: A MICROSCOPIC APPROACH, M. Fiałkowski, Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland.

We present an approach to the theory of viscosity of biaxial nematic liquid crystals based on the existing continuum theory [1] and show the method of obtaining microscopic formulas for viscosity coefficients. The derived formulas are expressed in terms of order parameters, temperature, number densities and diffusion constants. Obtained viscosity coefficients satisfy four Onsager-Parodi relations. Presented results are quite general because no assumptions about diffusion constants are applied and a very general form of an interaction potential is used. The only simplification concerns shapes of the molecules, which are modelled by ellipsoids with three different principal axes. In the limiting case, when an appropriate biaxial order parameter vanishes and system becomes uniaxial, we obtain the six Leslie viscosities involving, in general, two diffusion coefficients  $D_{\perp}$  and  $D_{\parallel}$  related to the rotational motion about short and long molecular axis, respectively and two ellipsoidal axis ratios. When the molecules possess symmetry axes, the formulas for the Leslie coefficients recover known results for uniaxial systems.

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## A1P.31

BI-AXIAL REPRESENTATION OF ORDER PARAMETERS, Swarnamala Sirsi and R Somashekar, Department of Physics, University of Mysore, Manasagangotri, Mysore 570006. India.

The two axes corresponding to the order parameters matrix  $S_{ij}$  are determined theoretically using the already known techniques [1,2] ie., the multiaxial parametrization of the polarization tensors characterising a spin assembly, in the context of nuclear physics. It is very well known that order parameter can either be expressed as a traceless, symmetric, second rank cartesian tensor or spherical tensor of rank 2,  $S_q^2$ , q = -2, -1, 0, 1, 2. Using the well known Wigner expression [3] for rotation matrices  $\mathcal{D}_{q'q}^2(\alpha, \beta, \gamma)$  any second rank tensor parameter can be taken to a frame where  $S_{\pm 2}^2 = 0$ . The ensuing quadratic equation is solved to yield two sets of polar angles which characterise the order parameter.

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- [2] G Ramachandran and V Ravishankar, J. Phys., G12, 1221 (1986).
- [3] M E Rose, Elementary theory of Angular momentum John-Wiley, New York, 1957.

A DETAILED MONTE CARLO INVESTIGATION OF A BIAXIAL SYSTEM, F. Biscarini<sup>1</sup>, C. Chiccoli<sup>2</sup>, P. Pasini<sup>2</sup>, F. Semeria<sup>2</sup> C. Zannoni<sup>3</sup>, <sup>1</sup> CNR - ISM 40121 Bologna, Italy - <sup>2</sup> INFN Sezione di Bologna 40126 Italy- <sup>3</sup>Dipartimento di Chimica Fisica ed Inorganica dell'Università, 40136 Bologna, Italy

We study a lattice system of biaxial particles interacting with a second rank anisotropic potential [1]. We have performed Monte Carlo calculations for a large number of different values of molecular biaxiality and we have determined a phase diagram for the system that we compare with molecular field predictions. A detailed investigation of the transition in the case of molecular biaxiality taking its limiting prolate-oblate dual value is also performed. Our results confirm the second order character of the nematic-isotropic in this case. The full set of relevant second rank biaxial and uniaxial order parameters is presented.

[1] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, C. Zannoni, Phys. Rev. Lett. 75 1803 (1995).

A1P.33

THEORY OF BIAXIAL NEMATIC ORDERING IN ROD-DISC MIXTURES REVISITED, A.G. Vanakaras and D.J. Photinos, Department of Physics, University of Patras, Patras 26500, Greece.

We review some basic experimental and theoretical results on orientational ordering in mixtures of thermotropic oblate and prolate mesoges. We then present new theoretical results for mixtures of hard rods and discs treated in the framework of the two-molecule cluster approximation. These results indicate that, depending on the relative strength of rod-disc interactions, a thermodynamically stable biaxial nematic mixture may be obtained. The complete isotropic-nematic phase diagram is studied for the case of purely hard-body interactions and also in the presence of additional site-specific interactions with different dispositions within the molecular frame of the rods and discs. The factors which promote the appearance of the biaxial mixture are discussed.

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A1P.34

THE GENERAL FREEDERICKSZ TRANSITION IN BIAXIAL NEMATIC FILMS, <u>H.Liu</u>, D.W.Allender\*, Department of Physics, Kent State University, Kent, OH, 44242,USA

Using Saupe's elasticity theory for biaxial nematics, we study the response of the triad of director fields in an external magnetic field under strong and weak anchoring boundary conditions. It is shown that under certain conditions, the directors will either undergo a Freedericksz transition or form a periodic pattern in a plane parallel to the plates of the liquid crystal cell. For four of different geometries distinguished by the surface alignment of the directors and the orientation of the external field, the corresponding threshold field for the Freedericksz transition or periodic pattern is obtained. These results reveal the relationship between the material properties and the external field, and suggest the feasibility of determining some of the elastic constants for biaxial nematics.

\* supported by NSF ALCOM Grant DMR 89-20147



#### APPLICATIONS OF LIQUID CRYSTALS TO LASER BEAM ANALYSIS

T. Vogeler, R. Bachmann, M. Kreuzer, N.V. Tabiryan\*, and T. Tschudi, Technische Hochschule Darmstadt, Institute of Applied Physics, Hochschulstraße 6, 64289 Darmstadt, Germany, \*Center for Research and Education in Optics and Lasers (CREOL), University of Central Florida, Orlando, FL, 32826, USA.

We present a nonlinear optical method to measure the intensity of a laser beam and the size and position of focal spots. It utilizes the orientational nonlinearity of liquid crystals (LC), the underlying physical mechanism being the light induced reorientation of LC molecules. Depending on its intensity an incidenting laser beam is self phase modulated leading to typical self diffraction patterns. These patterns and the dynamics of their appearance hold the required information.

Established laser diagnostic devices are able to measure power and/or energy and their spatial distribution to derive the intensity. In contrast our new method is direct, absorptionless and allows all-optical operation. For many applications this is of great interest since there the intensity of a laser beam is the main parameter to be known and controlled.

Both experimentally and theoretical we will show the dependence of measured parameters on the effect of interaction of light with LC and will discuss the extension to electro-optical schemes.

## A1P.36

SECOND HARMONIC GENERATION BY NEMATICS WITH PERIODIC DIRECTOR DEFORMATION, K.-M. Hsia, T. Kosa, P. Palffy-Muhoray and Y.S. Kim, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

Uniform nematics posses inversion symmetry, hence second harmonic generation (SHG) is forbidden in the dipole approximation. Weak SHG has been observed, however, experimentally [1,2,3], and an explanation has been put forward in terms of quadrupolar susceptibility. We report here studies of SHG in nonuniform nematics, whose director field varies in space. Optical buffing was used to obtain a periodic director deformation of the liquid crystal E7 with the wave vector in the plane of the cell walls. The alignment layer was polyimide doped with the azo dye Disperse Orange 3. The pump consisted of 38ps pulses at  $1.06\mu m$  from a mode-locked Nd:YAG laser. We have measured the intensity of the SH signal as function of angle as well as temperature, and studied the polarization. We discuss a simple microscopic model of the relevant mechanism, and compare the estimated conversion efficiency with experimental results. This work was supported by the NSF under ALCOM grant DMR 89-20147.

[1]M.E. Barnik, L.N. Blinov, A.M. Drozhkim and N.M. Shtyov, MCLC, 98, 1, 1983. [2]Ou-Yang Zhong-can and Xie Yu-zhang, Phys., Rev. A, 32, 1189, 1985. [3]M. Copic and T. Ovsenik, Europhysics Lett., 24, 93, 1993.

## A1P.37

THE CHIRALITY EFFECT ON THE OPTICAL NONLINEARITY OF SMECTIC C LIQUID CRYSTALS, Moojong Lim and Sin-Doo Lee\*, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

We have studied the chirality effect on the optical nonlinearity of smectic C (Sm C) liquid crystals (LCs) by means of the second-harmonic generation (SHG). The Sm C LCs used were a chiral SCE 13 and its racemic version SCE 13R, both of which have the Sm C phase at room temperature. A chiral agent S811 was added to SCE 13R for controlling molecular chirality which produces the optical activity. The SHG measurements were made on homogeneously aligned cells of SCE 13 and doped SCE 13R at an oblique incidence to the surface normal as a function of the azimuthal angle for rotation. From the electric field dependence of the optical nonlinearity, it was found that the chirality contributes to both the second-order and third-order nonlinearities which couples with a static electric field.

<sup>\*</sup>Supported in part by Samsung Display Devices.

PYROELECTRIC LIQUID CRYSTAL POLYMERS (PLCP'S) FOR SECOND-HARMONIC GENERATION PREPARED FROM FERROELECTRIC LIQUID CRYSTALLINE ACRYLATE MONOMER MIXTURES. M. Trollsås<sup>a</sup>, F. Sahlén<sup>a</sup>, A. Hult<sup>a</sup>, U. W. Gedde<sup>a</sup>, C. Orrenius<sup>b</sup>, T. Norin<sup>b</sup>, <u>D. Hermann</u><sup>c</sup>, P. Rudquist<sup>c</sup>, S. T. Lagerwall<sup>c</sup>, L. Komitov<sup>c</sup>, B. Stebler<sup>c</sup>, J. Lindström<sup>d</sup> and O. Rydlund<sup>d</sup>. <sup>a</sup>Department of Polymer Technology, Royal Institute of Technology, S-100 44 Stockholm, Sweden; <sup>b</sup>Department of Chemistry, Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden; <sup>c</sup>Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden; <sup>d</sup>National Defence Research Establishment, S-172 90 Stockholm, Sweden.

We present a comparison of the non-linear optical properties in terms of the Pockels effect and of second-harmonic generation in Pyroelectric Liquid Crystal Polymers. These are made by crosslinking ferroelectric liquid crystalline acrylate monomer mixtures by in situ UV-photopolymerization. The spontaneous polarization is compared between the monomer mixtures and is related to the non-linear optical activity of the corresponding PLCP. The former ranges between 20 and 200 nC/cm<sup>2</sup>, and the latter between roughly 0.15 and (15-35) pm/V in terms of the Pockels coefficient  $r_{22}$ - $r_{12}$ . A comparison between direct second-harmonic generation measurements will also be presented. We have found that the magnitude of these properties is closely related to the amount of chiral substance in the material.

A1P.39

NONLINEAR OPTICAL PROPERTIES OF THE THERMOTROPIC LIQUID CRYSTALLINE MAIN-CHAIN POLYMERS (AROMATIC POLYESTERS) AND THEIR APPLICATIONS, T. Asada. Department of Polymer Chemistry, Kyoto University, Kyoto 606, JAPAN.

To get a durable and good nonlinear optical materials, the second harmonic generations of the liquid crystalline main-chain type copolymers of 2-hydroxy-6-naphtoic acid (HNA) with 4-hydroxy-benzoic acid (PHB), with various composition ratios were studied[1]. Investigation on the relation between molecular compositions and the hyperpolarizability ( $\beta$ ) has been performed by Molecular Orbital Methods. The molecular simulation method clearly supports the idea that the high SHG of a main-chain polymer is mainly originated the additivity of  $\beta$  value of individual unit due to head to tail connection. It was proved experimentally that the mechanical extension and poling are effective to improve the SHG efficiencies. Electro-optical properties and applications for photonics elements of the sample will also be introduced. [1] T. Asada, Mol. Cryst. Liq. Cryst., 254, 125(1994).

A1P.40

THE STUDY OF THIRD ORDER OPTICAL NON-LINEARITIES OF NEMATIC LIQUID CRYSTAL, Jianxin Guo, Jing Ma\*, Shumei Wuang\*, Zhenjun Ma, Ximin Huang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021; Laboratory of Excited State Processes, Academy of Sciences, Changchun 130021\*

The third order optical non-linearities of a nematic liquid crystal have been studied with Z-scan technique<sup>[1]</sup> using picosecond pulses. The samples were planar alignment liquid crystal cells with different thicknesses. We detected the self-focussing characteristics of polarized light for different directions. The nonlinear refractive index and the nonlinear absorption coefficient have been got using the fitting method with the theory curve. The mechanism of the large third order optical nonlinearities have been discussed. The dominant mechanism most probably arise from the electronic contribution and the molecular reorintational contribution.

[1] Sheik-Bahae, etal., IEEE.J.Quant.Electron., 26, 760 (1990).



DIELECTRIC RELAXATION AND NEMATIC POTENTIAL OF SOME NEMATO-GENIC COMPOUNDS, S R Kumarswamy, R Somashekar, M S Madhava and D Revannasiddaiah, Department of Physics, University of Mysore, Manasagangotri, Mysore 570006, India.

Component of  $\epsilon_{\parallel}$  of dielectric tensor has been studied in the nematic phase of four nematogenic compounds namely, 60CB, 70CB, IPBOC, 6CHBT. Using the relaxation data we have estimated the nematic potential associated with the above molecules, based on Maier and Saupe mean field theory.

#### A1P.42

ORDER PARAMETER AND DISTRIBUTION FUNCTIONS FOR NEMATOGENIC OBA AND NBA, A P Divya, K Narayanamurthy, M S Madhava, D Revannasiddaiah and R Somashekar, Department of Physics, University of Mysore, Manasagangotri, Mysore 570 006 India.

Using refractive index and density data for nematogenic compounds OBA and NBA, orientational order and hence distribution functions have been determined. From this, the higher order parameter <P4> has been estimated for these two compounds. The physical interpretation of these parameters <P2> and <P4> has been given in terms of statistical quantities like 'variance' and 'kurtosis'.

## A1P.43

PROPAGATION OF SOLITONS IN A NEMATIC OPTICAL FIBER\*, R.F.Rodríguez and J. A. Reyes, Departamento de Física Química, Instituto de Física, U.N.A.M., A.P. 20-364, 01000 México, D.F., México.

We have studied the propagation of a wavepacket of TM modes through a planar multimodal waveguide with a nematic core. In the weakly nonlinear limit (Kerr medium) and when attenuation effects are small, we show that the dynamics of the optical waves is described by the Nonlinear Schördinger Equation and that the wavepacket propagates as optical solitons along the central part of the cell [1]. Using experimental measurements of the dispersion relation for MBBA, we calculate the nonlinear refraction index as a function of the incidence angle and the power required to generate these solitons. The former shows a large optical nonlinearity and the latter is as low as a tenth of a miliwatt.

[1] R.F. Rodríguez and J. A. Reyes, Mol. Cryst. Liq. Cryst. 1996 (to be published)

\* Supported by DGAPA-UNAM IN100494

SECOND HARMONIC GENERATION BY SURFACE POLARIZATION OF ELECTRIC PERMITTIVITY IN NEMATIC LIQUID CRYSTAL, K. -M. Hsia, R. Klouda, O. Lavrentovich and P. Palffy-Muhoray\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA. Second harmonic generation (SHG) from the surface of liquid crystals has been extensively studied. Using the surface polarization gradient of electric permittivity from the different surface coating materials can be one mechanism to break the centrosymmetry of the nematics and to stimulate the nonlinear frequency doubling. We present here the results of surface SHG by polarization gradient in 5CB sandwiched between two different coating materials. The sample's thickness is 23 um and both sides have the homeotropic alignment. The incident laser wavelength is 1.06 um generated by a 38 ps YAG laser. The surface SHG is first verifyed by a wedged sample, in which the Intensity of SH signal doesn't change with the thickness. It is found that the SH signal comes from both the transmitted and the reflected directions with comparable intensity. Different coating materials and configurations have been used to generate the SH signal and to compare their effectiveness. The angular dependence of SHG by surface polarization gradient has also been measured.

[1] O. D. Lavrentovich, et al, Sov. Phys. JETP 72(3), March 1991.

\*Supported by NSF under ALCOM grant DMR89-20147.

A1P.45

A UNIMODAL NEMATIC WAVEGUIDE\* <u>J. A. Reyes</u> and R. F. Rodríguez, Departamento de Física Química, Instituto de Física, U.N.A.M., A.P. 20-364, 01000 México, D. F., México.

A model for a planar unimodal nematic cored waveguide is discussed. In previous work [1] we have studied a multimodal planar waveguide which exhibits a waveguide effect that concentrates the ray trajectories in the central part of the cell. In this work we show that for the WKB limit the same waveguide effect exists for the case where the guide is single modal. We derive the condition to have a unimodal waveguide and for MBBA and 5CB we calculate the spatial distribution of the electromagnetic energy density in the absence of hydrodynamic flows. We show that this energy is concentrated between two caustics in the central part of the cell.

[1] J.A. Reyes and R.F. Rodríguez, J. Nonlin.Opt. Phys. Mater. 4, 943 (1995) \* Supported by DGAPA-UNAM IN100494

A1P.47

ORIENTATIONAL RELATIONSHIP AMONG POLYIMIDE ALIGNMENT LAYER, LIQUID CRYSTAL MONOLAYER AND BULK PRETILT ANGLE, K. Shirota, M. Yaginuma, T. Sakai, K. Ishikawa, H. Takezoe and A. Fukuda, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan.

We have determined the orientational distribution function (ODF) of side chains of rubbed polyimide (PI) films and liquid crystal (LC) monolayers on those films (PI & LC) by optical second-harmonic generation (SHG). To separate the SHG signal of the LC monolayer from that of the (PI & LC) film, the phase difference between the SHG signals from PI and (PI & LC) was measured by an interference method. We found that the ODFs of PI and LC films are quite different. However, serious changes in these ODFs occur at the same rubbing strength, where the pretilt angle also shows a remarkable change.



ORIENTATIONAL INTERACTION OF LIGHT WITH AZODYEDOPED NLC D.B.Terskov<sup>1)</sup>, A.S.Zolot'ko<sup>1)</sup>, M.I.Barnik<sup>2)</sup>, V.G.Rumyantsev<sup>2)</sup>. 1) P.N.Lebedev Physical Institute of the

Russian Academy of Sciences, Leninsky pr.53, Moscow, 117924, Russia, 2) Russian State Center of Science "Organic Intermediates and Dyes Institute", ul.Bol'shaya Sadovaya 1-4, Moscow, 103787, Russia

The large light induced director reorientation in NLC, doped with extremely small amounts (~0.01wt%) of azodyes, was observed at light beam power ~ 1 mW.

It was found that the reorientation direction depends on the direction of the light wave propagation, its wavelength and also on the crystal temperature [1].

It was established that azodyedoped NLC exhibits orientational bistability in relation to the direction of light propagation. A simple model of this bistability is proposed [2].

The polarization properties of the aberration pattern, accompanying the director reorientation in azodyedoped NLC, were investigated.

- [1]. M.I.Barnik, A.S.Zolot'ko, V.G.Rumyantsev and D.B.Terskov, Crystallography reports, v.40, 691, 1995.
- [2]. D.B.Terskov, A.S.Zolot'ko, M.I.Barnik, and V.G.Rumyantsev, Mol.Mater. (in press).

A1P.49

SECOND HARMONIC GENERATION FROM CHIRAL SMECTICS: SOME NEW EFFECTS, S. Sprunt, R. Geer, B. Ratna and R. Shashidhar, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242 and Code 6900, Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington DC 20375

Second harmonic generation (SHG) from ferroelectric smectic- $C^*$  (Sm- $C^*$ ) phase is an active area of research. The main thrust in this area is to design molecules with a high molecular  $\beta$  and achieve a large macroscopic second order non-linear optic coefficient. We have recently observed two new effects: (i) SHG in the chiral smectic-A phase and (ii) Enhanced SHG in a crystal phase due to periodic modulation of the refractive index achieved by cooling a Sm- $C^*$  phase in the presence of the electrical field. The results are compared with those in the Sm- $C^*$  phase.

A1P.50

THERMOMECHANICAL EFFECT IN LIQUID CRYSTALS

M.I.Barnik<sup>1)</sup>, V.F.Kitaeva<sup>2)</sup>, V.G.Rumyantsev<sup>1)</sup>, and A.S.Zolot'ko<sup>2)</sup>. 1) Russian State Center of Science "Organic Intermediates and Dyes Institute", ul.Bol'shaya Sadovaya 1-4, Moscow, 103787, Russia, 2) P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Leninsky pr.53, Moscow, 117924, Russia

The pecularities of interaction of narrow laser beam with homeotropic nemaic liquid crystal (NLC), doped with dyes, and with homeotropic smectic A iquid crystal (SLC), being in the region of its transition to nematic phase, were investigated.

It is established that director field deformattion, being axially symmetrical or almost axially symetrical, is formed in these crystals under the influence of light. In NLC at the beam power, slightly exceeding deformation threshold value, the director field oscillations are excited. In SLC the deformation is "frozen up" during the crystal cooling.

The appearence of deformation is explained by director reorientation under the influence of inhomogeneous temperature field (thermomechanical effect).

THEORY OF SECOND HARMONIC GENERATION IN PERIODIC FERROELECTRIC MATERIALS, <u>David S. Moroj</u>\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242 and David E. Zelmon, Material Directorate, Wright Laboratory, Wright-Patterson AFB, OH 45433, USA.

Second harmonic generation is investigated in periodic ferroelectric materials. A model of the nonlinear dielectric susceptibility for a chiral smectic C liquid crystal is constructed in terms of the director of the chiral molecule, the unit vector perpendicular to the smectic layers and their vector product. The electric field is expanded in a Fourier series having the same periodicity as the ferroelectric material. The Fourier components, or the amplitudes of the electric field in various modes, satisfy a five term vector recursion relation and the solutions are obtained by iteration for small tilt angles. The electric field for the second harmonic in the nonlinear medium is expanded into a Fourier series with slowly varying amplitudes. In the lowest order approximation, it is shown that the second harmonic electric field is given by a product of the linear solution multiplied by the leading term of the Fourier series which is calculated using the slowly varying envelope approximation.

[1] D. S. Moroi, Technical Report to Dept. of Air Force, Oct., 1995.

\* Supported by the 1994-95 University Resident Research Program, AFOSR.

A1P.52

SECOND HARMONIC GENERATION IN A LIQUID CRYSTAL WITH PERIODIC DIRECTOR VARIATION, <u>David S. Moroi</u>, K.-M. Hsia and P. Palffy-Muhoray, Liquid Crystal Institute & Dept. of Physics, Kent State University, Kent, OH 44242, USA.

We have investigated second harmonic generation in a liquid crystal with periodically varying director. In this theory, we have used a model where the dielectric tensor varies sinusoidally in one direction. The second order nonlinear dielectric susceptibility is obtained by contracting the nonzero third order susceptibility with a constant spontaneous electric field caused by inhomogeneity of the material. The second harmonic electric field is calculated using a Fourier expansion and a slowly varying envelope approximation. We show that, to lowest order, the second harmonic electric field is proportional to the product of the linear solution and the field calculated in the slowly varying envelope approximation. There are eight possible phase matching conditions, one of which gives rise to the maximum second harmonic intensity.

[1] D. S. Moroi, Technical Report to Dept. of Air Force, Oct., 1995. \*Supported by NSF under ALCOM grant DMR89-20147.

A1P.53

BACKFLOW EFFECTS ON OPTICAL PROPERTIES OF NEMATIC LIQUID CRYSTALS<sup>1</sup>. R.F. Rodríguez\*, Instituto de Física, UNAM, P. Ortega, Facultad de Química, UNAM, R. Diaz-Uribe\*, Centro de Instrumentos, UNAM, and J.A.E. Roa-Neri, UAM-Azcapotzalco, México, D.F., México

We present a model of a nematic liquid crystal cell to describe the early and final stages of the reorientation process induced by the action of an obliquely incident optical field. The presence of hydrodynamic backflows associated with the reorientation in both, a homeotropic and planar geometry, is explicitly taken into account. We study the effect produced by these backflows on two specific optical properties of the nematic, namely, its phase change and its inverse focal lenght. These quantities are calculated analytically and evaluated for the nematic phase of CBOOA. It is shown that for these two configurations, hydrodynamic backflows may produce significant, and in principle, measurable changes as high as 75% in these properties.

\* Fellow of SNI

<sup>&</sup>lt;sup>1</sup> Partially supported by DGAPA-UNAM, project IN100494.



PHASE CONJUGATION SELF-OSCILLATION IN A QUASI-STATIC ELECTRIC FIELD BIASED NEMATIC LIQUID-CRYSTAL FILM, <u>Shu-Hsia Chen</u> and Yuhren Shen, Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, 300, ROC.

We report a theoretical study of the self-oscillation of phase conjugation in a quasi-static electric field biased nematic liquid-crystal film. The molecular reorientation mechanism and degenerated four wave-mixing scheme were used for getting the phase conjugate reflectivity in a planar aligned nematic film. From the continuum theory, we obtained the distribution of molecular reorientational angle and the refractive index variation under the small orientational angle approximation. Substitution the refractive index variation into the Maxwell's wave equation, we got the set of four coupled wave equations. Under the undepleted-pump approximation, we obtained the analytic solution of phase conjugate reflectivity and found the criterion of phase conjugation self-oscillation as the reflectivity goes to infinity.

[1] Iam-Choon Khoo, Yang Zhao, IEEE J. Quantum Electron. 25, 368 (1989).

#### A1P.55

NONLINEAR OPTICAL PROPERTIES OF METALLORGANIC FERROELECTRIC LIQUID CRYSTALS, J. Ortega, C.L. Folcia\*, J. Etxebarria\*, R. Iglesias†, M.B. Ros†, J.L. Serrano†, L. Díez§, P. Espinet§, J.A. Miguel§, Física Aplicada II, \*Física de la Materia Condensada, Universidad del País Vasco, 48080 Bilbao (Spain), †Química Orgánica, Universidad de Zaragoza, 50009 Zaragoza (Spain), §Química Inorgánica, Universidad de Valladolid, 47005 Valladolid (Spain)

The SHG efficiency has been investigated in Pd and Pt-containing FLC's. The studied materials are orthometallated β-diketonate and dimeric complexes. Although none of the compounds possesses well-defined donor-acceptor arrays, the NLO efficiencies have been found to be above 10<sup>-2</sup> pm/V in all cases. The second-order susceptibility tensor has been completely determined as a function of temperature in the Sc\* phase of one of the compounds. The NLO coefficients reach values as high as d23=0.12 pm/V. The results have been interpreted qualitatively taking into account the molecular structure. A comparison with traditional organic FLC's has been also carried out. Design considerations indicate that metal-containing FLC's could offer better prospects for NLO applications.

#### A1P.56

NEMATIC LIQUID CRYSTALS WITH POLAR ORDERING FORMED FROM SIMPLE AROMATIC POLYESTER, T. Watanabe, S. Miyata, T. Furukawa<sup>1</sup>, H. Takezoe<sup>1</sup>, T. Nishi<sup>2</sup>, M. Sone<sup>2</sup>, A. Migita<sup>2</sup> and <u>J. Watanabe<sup>2</sup></u>, Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Nakamachi, Koganei-shi, Tokyo 184, Japan, <sup>1</sup>Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan, <sup>2</sup>Department of Polymer Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan.

We describe a distinct nematic liquid crystal with polar ordering which is formed from the polar rod-like aromatic copolyester comprising the 4-hydroxy benzoic acid and 6-hydroxy-2-naphthoic acid. The polarity in the nematic phase appears along the nematic director as determined by the second-harmonic generation. It was found that the SHG activity appears in compounds with high degree of polymerization. This fact suggests that the strong dipole-dipole interaction between polar rod-like molecules is the origin of the polar structure.



DIRECTOR SLIDING OVER ISOTROPIC RIGID SURFACE AT LIGHT-INDUCED UNWINDING OF CHIRAL NEMATIC LIQUID CRYSTAL, A.G.Iljin and Yu.A.Reznikov, Institute of Physics, Natnl.Acad.Sc., Prosp. Nauki 46, Kiev 252022 UKRAINE

The chirality of the system - nematic LC + photosensitive twisting agent - appeared to undergo extremely high changes under the light action, resulted in a drastic increase of intrinsic cholesteric pitch [1]. When the latter is greater then cell thickness, surface - LC molecules interaction opposes the helical pitch untwisting displaying so called "surface memory effect" [2]. However, this helix relaxation rather often takes place causing LC director rotation on the isotropic substrate surface. Characteristic times of such a rotation (10 - 100 s) are much greater than that of director volume relaxation and of chiral agent photochanges. These times and, moreover, the existense of rotation are essentially dependent on both the type of orienting surface and LC composition. Dynamics of observed phenomenon is guided by the surface interaction with LC molecules and could be associated with many as macroscopic as microscopic parameters (surface memory, roughness, adsorption, etc.). We believe the investigation of the new one - "surface rotation viscosity" (parameter corresponding to the concrete surface-LC pair) being the effective method to characterize the anchoring features of the surface.

[1] A.Iljin et al, Mol.Cr.Liq.Cr. 261, 159 (1995). [2] N.A.Clark. Phys.Rev.Lett., 55, 292 (1985).

A1P.58

NONLINEAR OPTICAL AND PYROELECTRIC PROPERTIES OF NITROBIPHENYL CONTAINING POLAR LANGMUIR-BLODGETT FILMS, T. Srikhirin, D.-Y. Minh Nguyen, S.H. Ou, J.A. Mann, J.B. Lando, D. Schuele, L. Zhou., S. Hubbard, and K.D. Singer, Departments of Macromolecular Science and Physics, Case Western Reserve University, Cleveland, Ohio 44106.

Nonlinear optic and pyroelectric studies were carried out on polar Langmuir-Blodgett films fabricated from siloxane copolymers containing mesogenic side-chains. One of the side chains is a nitro-substituted biphenyl showing second-order nonlinear optical properties while the other is incorporated to enhance the spreadability and deposition. X-ray diffraction, second harmonic generation measurements and pyroelectric studies all support the existence of polar structure in multilayer films with the polar axis nearly perpendicular to the substrate. The second harmonic coefficient was measured to be 42 pm/V. Unusual pyroelectric and dielectric responses were observed indicating a transition near room temperature in the presence of an electric field. The magnitudes of the pyroelectric coefficients were determined to be between 2.0 and 3.0  $\times 10^{-10} C/(cm^2 \cdot ^{\circ}C)$ . FTIR-RA studies confirm the liquid crystalline structure, as do texture photomicrographs. Optical waveguides were fabricated with 135 monolayers, and optical losses and mode indices were measured.

A1P.59

LIQUID CRYSTAL MODULATOR OF LASER RADIATION FOR HIGH-POWERED LASERS OF INFRA-RED RANGE OF SPECTRUM, Z.Mikityuk, J.Semenova, M.Nutskovsky, O.Sushinsky, State University "Lvivska Politechnika", Bandera Str., 12, Lviv, Ukraine, 290646.

The new method of creation of liquid crystal light modulators high-powered laser radiation in infra-red range of spectrum on the proposed. base of cholesteric-nematic phase transition is modulation carries out by two stages: on the stage liquid first crystal is put into working state by means of heat absorption; on transition the second stage the cholesteric-nematic phase effect. is using for laser radiation modulation. The recommendations for liquid crystal mixture content optimization and for modulator for wavelength 1,06 mm are elaborated.



ENERGETICS OF SOME DEFECTS IN BIAXIAL NEMATICS, Sreejith Sukumaran, and G.S.Ranganath, Raman Research Institute, Bangalore 560 080, India.

Using Saupe's continuum theory of biaxial nematics [1], we describe analytically the structure and energetics of some non-singular wedge and hybrid disclinations [2]. We show that certain non-singular hybrid disclinations can be energetically favourable compared to singular half-integer disclinations. We find that the nature of interaction between singular hybrid disclinations depends not only on the sign of defects but also on the elastic anisotropy due to inherent biaxiality. Defects in spherical droplets [3] are also considered. From energetics we find a transformation, on increase of size, from a Dirac monopole with a tetrahedral arrangement of disclination lines to a boojum.

- [1] A.Saupe, J.Chem.Phys., 75,5118 (1981)
- [2] G.S.Ranganath, Current Science, 57,1 (1988)
- [3] N.D.Mermin, Rev.Mod.Phys.,51,591 (1979)

## A1P.61

DYNAMIC HOLOGRAMS WITH WAVE FRONTS WRITING IN A BLEACHABLE DYES ACTI-VATED LIQUID CRYSTALS, Svetlana V. Serak, A.A. Kovalev, and G.L. Nekrasov, Institute of Electronics, Byelarus Academy of Science, 22, Logoiski Tract, Minsk 220090, Byelarus.

We demonstrated earlier the possibilities of bleachable dyes activated LC as media for controlled passive filters of ruby and neodimium lasers [1] and WFC-mirrors [2]. In this report the peculiarities of conjugated wave forming in dynamic holograms induced in phototropic LC-media on the different optical nonlinearities by nanosecond laser pulses are considered. The kinetics of gratings on the dyes bleaching, thermal processes, molecular reorientation of both dye and LC in cyanobiphenyls layers with thickness from 50 to 100 mkm, doped by phtalocyanine, bisantene and antraquinone dyes is investigated by using probe radiation of cw gas laser. The wave front conjugation was observed when the pump intensity varied from  $0.01 \ J/cm^2$  to  $1 \ J/cm^2$ . At the highest value the stable disclination in the LC-layer was appeared. The enhanced reflection of conjugated wave on the thermal nonlinearity near the phase transition nematic-isotropic liquid was obtained.

- [1] A.A.Kovalev, G.L.Nekrasov, and S.V.Serak, MCLC.193, 51 (1990).
- [2] A.A.Kovalev, S.V.Serak, N.A.Usova, G.L.Nekrasov and T.A.Davidovich, MCLC. 256, 271 (1995).

## A1P.62

ELECTRONIC AND GEOMETRIC STRUCTURE MODELLING OF THE SERIES OF SUB-STITUTED CYANODIPHENYLE AND DYE ADMIXTURES, V.I.Beresin, N.B.Zotov, V.P.Sevost'yanov, G.N. Ten, Saratov State University 410071, Saratov, Astrakhanskaya st., 83, Russia.

The investigation of geometric and electronic structure of the series of substituted cyanodiphenyle: 5CB, 3OCB, 5OCB and dye admixtures: 4-(4-nitrophenyl)4'-(4-N, N-diocthylaminophenylaso) asobensee, 4-etylamino-4- (n- cyanophenyl) asobensee was carried out by means of quantum chemistry methods (PM3, CNDO/S). The structural ordering of dye admixtures was modelled for the planar-orientated liquid crystals (LQ) as "LQ-dye" pair approximation. The intermolecular interactions of "LQ-dye" were estimated by means of atom-atom potentials method using 6-exp potential. Both the electronic absorption spectra of the compounds investigated for the case of isotropic solution and the polarization spectra of the dyes long wavelength absorption band in the planar-orientated liquid crystals were measured. The satisfactory agreement between the calculated and experimentally founded electronic transitions energies was achieved. The correspondence of the dyes structural ordering in orientated liquid crystals, which was estimated according to the absorption band dichroism, to the modelling calculations of the molecula "LQ-dye" pair conformations for atomic aproximation was obtained.

ON THE RELATION BETWEEN CONTINUUM APPROACHES OF NEMATICS, M. NAKAGAWA, Department of Electrical Engineering, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata 940-21, JAPAN

We have elucidated the relationship between vector[1-3] and tensorial[4,5] approaches for elasto-dynamics of nematics within the framework of continuum theory. It will be elucidated that certain Lagrange multipliers have to be substantially involved even in the tensorial framework as well as the vector one to assure the equivalence between two approaches. A contraction for the indices in the time-dependent Landau-de Gennes equation in a tensorial form will be found to be eventually recasted into the Ericksen-Leslie equation[6,7] without flow dynamics.

In practice, denoting the molecular field as  $h_{ij}$ , we have concentrated our interests on the following time-dependent Ginzburg-Landau equation for nematics with a tensor order parameter  $a_{ij}$ , expressed in terms of

 $\gamma \frac{\partial a_{ij}}{\partial t} = h_{ij} + v_{0} \delta_{ij} + v_{1} a_{ij} + \lambda a_{mn} a_{im,k} a_{jn,k} + (\mu_{ij} - \mu_{ji}) .$  [1] C. W. Oseen: Trans. Faraday Soc. **29**(1933)883. [2] H. Zocher: Trans. Faraday Soc. **29**(1933)945. [3] F. C. Frank: Discuss. Faraday Soc. **25**(1958)19.[4] P. G. de Gennes: *The Physics of Liquid Crystals* (Oxford University Press, 1974).[5] P. Sheng and E. B. Priestly: *Introduction to Liquid Crystals* ed. E. B. Priest, P. J. Wojtowicz and P. Sheng, (Plenum Press, 1976).[6] J. L. Ericksen: Trans. Soc. Rheol.5(1961)23.[7] F. M. Leslie: Proc. Roy. Soc. London, Ser. **A307**(1968)359.

A1P.64

#### VISCOSITY OF UNIAXIAL NEMATICS AND CLUSTER MODEL

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We study the viscosity of uniaxial nematic LC on the basis of the cluster approach, which starts from the model assuming the existence of ellipsoidal clusters in LC, every one of which is placed into incompressible medium. Resolving the problem of ideal liquid flow we have got the expression for the velocity field. Leslie viscosities were derived in dependence on the cluster m.-g. size d and on its anisometry  $\kappa$  with the assumptions that the energy diffusion was due to the friction of the liquid about the cluster. Correlation was analyzed between our theory and experimental data for MBBA, 5CBP, N4 and EM LC which made it possible to determine the change of d and  $\kappa$  in temperature. We found that the cluster size may be approximized with exponential function  $d = \exp\left(c_0 - c_1 \frac{T}{T_{NI}}\right)$ . The behavior of  $\kappa$  in temperature is similar to that of the order parameter (as a "cluster order parameter"  $S_{clust}$  we used the claster eccentricity)  $S_{clust} = (1 - \frac{T}{T^*})^{\beta}$ . The accuracy of our approach was proved to be in the bounds of 10%. So the proposed theory taking into account the short-range correlations enabled us to get the analytical expressions for the Leslie viscosities and to make some important conclusions of their temperature dependences.

ANTIFERROELECTRIC ACHIRAL MESOGENIC POLYMER, E.A. Soto Bustamante\*, S.V.Yablonskii\*\*, B.I.Ostrovskii\*\*, L.A.Beresnev\*, L.M.Blinov\*\*, and W.Haase\*\*, \*\*Institute of Physical Chemistry, THD, Petersenstr.20, Darmstadt, 64287, Germany, \*\*Institute of Crystallography, RAS, Leninsky pr.59, Moscow, 117333 Russia.

The X-ray structure determination, pyroelectric and piezoelectric measurements have been carried out on mesogenic mixtures composed of achiral side-chain polymers and their monomers. Certain mixtures show antiferroelectric polarization hysteresis loops in the mesophase while the two components of the mixtures taken alone show no antiferroelectricity. By X-ray analysis the mesophase was shown to be a bilayered smectic C with liquid like layers. The results obtained on polymer-monomer mixtures are interpreted in terms of the smectic C structure with alternating tilt which, from the symmetry viewpoint, is allowed to be antiferroelectric. The macroscopic polarization measured in the mesophase reaches the values about 300nC/cm<sup>2</sup>. The mixtures, being cooled to the glassy state under a d.c. electric field applied, reveals high pyroelectric coefficient comparable to that observed in proper polymer ferroelectrics and perspective for application in radiation detectors.

A2P.02

A STUDY OF SILOXANE HEAD GROUPS AND SPACERS IN CALAMITIC LIQUID CRYSTALS, <u>Petra Kloess</u>\*, H.J. Coles\*, D. Guillon \*Liquid Crystal Group, Physics Department, University of Southampton, SO17 1BJ, UK # IPCMS, 23 rue du loess, BP 20 CR, 67037 Strasbourg, France

It is well known that using a siloxane spacer or head group instead of a polymer backbone in ferroelectric materials leads to low viscosities and fast switching.[1]. For two different kind of mesogens, biphenyl benzoate and cholestanol, we determined the influence of the siloxane on the phase behaviour and the properties. We altered te shape of the siloxane group to determine the influence a) on a ferroelectric system and b) on the phase behaviour on a cholesteric system. Besides several monodisperse mono- and bimesogenic compounds, two polydisperse bimesoges were synthesised and characterised.

H. Coles, H. Owen, J. Newton, P. Hodge Liq. Cryst. 15, 5, 1993

A2P.03

HOT FERROELECTRIC LIQUID CRYSTALS

<u>William N. Thurmes</u>, Michael D. Wand, Kundalika M. More, and Rohini T. Vohra,
Displaytech, Inc., 2200 Central Avenue, Boulder, CO 80301

Liquid crystals which exhibit mesomorphic phases at high temperature are useful for, among other purposes, broad temperature pressure sensors. In an attempt to design high-temperature smectic C phase materials, we synthesized a variety of mesogenic oligomers and polymers. We obtained, to our knowledge, 1) the first carbon-based smectic C main chain polymer, 2) the first imide-containing smectic C liquid crystal, 3) the highest temperature smectic C phase reported (236°C), and 4) the highest temperature smectic A phase reported (304°C). This work was supported by NASA grant NAS1-20143.



DYNAMIC PYROELECTRIC BEHAVIOR IN THE SMECTIC-C\* PHASE OF LIQUID CRYSTALLINE TERPOLYMERS, R. Geer, J. Naciri, B. Ratna and R. Shashidhar, Code 6900, Center for Bio/Molecular Science& Engineering, Naval Research Laboratory, Washington DC 20375.

We report the dynamic pyroelectric behavior of a new class of liquid crystalline polymers - terpolymers, wherein two types of mesogenic groups as well as a methyl group are attached to a siloxane backbone. The ratio of the side groups has a dramatic effect on the temperature dependence of the pyroelectric coefficient (p), in some cases p showing no dependence on temperature. It is also shown that the terpolymers retain their property even for submicron films. The importance of these results for the development of uncooled IR sensors is discussed.

## A2P.05

OPTICAL ANISOTRPY AND COFORMATION OF POLY (FLUORALKOXYPHOSPHAZENES) IN SOLUTIONS, I.N. Shtennikova, G.F. Kolbina, D.R. Tur, Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Peterburg, Bolshoy 31, 199004, Russia.

Conformational and optical propetries of some poly (fluoralkoxyphosphazenes) (PF) were invistigated by birefringenes and viscometry. Studied polymers having non organic main chain and the ability to organize the thermotropic mesofphase differ from each other by the side chaine length:

Comparative researches of optical anisotropy dependence of PF molecules on the side chaine lenght were carried out in one solvent (refractive index of which is close to that of polymer). It is established that shear optical coefficient  $[\eta] / [\eta]$  of PF molecules essentially depends on the linght and structure of the side chain. It shown that the nature of the solvent used considerably influenced the values  $[\eta] / [\eta]$  and intrinsic viscosities PF-2 molecules.

The dependence of rotatory diffusion coefficient and optical anisotropi of PF-2 molecules on molecular weights was studied in wide range.

#### A2P.06

ORIENTATIONAL ELASTIC CONSTANTS OF POLYMER COMBLIKE NEMATICS, A.P.Filippov and L.N.Andreeva, Institute of Macromolecular Compounds of R.A.S., Bolshoi pr. 31, St.Petersburg, 199004, Russia, and E.B.Barmatov and V.P.Shibaev, Chemistry Department, Moscow State University, 119899, Moscow, Russia.

Elastic deformations of uniformly orientated layers of thermotropic polymeric comblike nematic in magnetic field were studied using the method of Freedericks transitions. The temperature dependences of splay and bend elastic constants and optical anisotropy (and correspondingly, the degree of orientational order) were determined. The bend constants and the splay constants were obtained by the independent investigations of the deformations of the homeotropic and planar textures, correspondingly. On changing the relative temperature from -0.5 to -65 degrees, the optical anisotropy increaces from 0.05 to 0.1. This experimental fact shows double increase of order parameter. The values of elastic constants are of the same order with those for low molecular weight nematics and polymer nematics investigated previously. It was found that in investigated temperature range the splay constant values are slightly more then the bend constant values.

POLYMERIZATION OF DISCOTIC LIQUID CRYSTALLINE TRIPHENYLENES, Ingo Bleyl†, Christian Erdelen‡, Jürgen Simmerer†, Dietrich Haarer†, Hans-Werner Schmidt‡, Experimental Physics IV† and Macromolecular Chemistry I‡, 95440 University of Bayreuth, Germany; Wolfgang Paulus, BASF AG, Ludwigshafen, Germany

Liquid crystalline triphenylenes show photo-induced hole conductivity with mobilities of  $\mu=10^{-3} {\rm cm}^2/{\rm Vs}$ . In a higher ordered phase the mobilities are even two decades faster [1]. This property makes triphenylenes suitable for technical applications as transport material for the xerography process. It is therefore necessary to stabilize the mesophase in a polymer or a molecular network. We have investigated the influence of the polymerization of substituted triphenylenes on the degree of order and on the transport properties. We have obtained these data by conventional time-of-flight techniques. Our experiments show, that the polymerization itself disturbs the mesophase profundly and reduces the mobility to values below  $10^{-4} {\rm cm}^2/{\rm Vs}$  at room temperature. One substitution scheme allows mobilities of more than  $10^{-2} {\rm cm}^2/{\rm Vs}$  in the unpolymerized state; this may be a promising approach to a polymeric material with high mobilities.

[1] D. Adam, P. Schuhmacher, J. Simmerer, L. Häußling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* 371, 141 (1994)

A2P.08

IN-SITU PHOTOPOLYMERIZATION OF DISCOTIC LIQUID CRYSTALLINE ACRYLATES IN THE NEMATIC DISCOTIC PHASE. Christine D. Favre-Nicolin, Johan Lub, Paul van der Sluis, Philips Research (WB 61), Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

Discotic liquid crystals (DLCs) exhibiting the nematic discotic phase ( $N_D$ ) are good candidates to make optical compensation layers to improve the viewing angle of twisted nematic liquid crystal displays. The relative fluidity of the  $N_D$  phase together with the disk-shape of DLCs leads to a spontaneous homeotropic alignment of these materials between substrates, a direct way to obtain thin films with a negative birefringence. However, the extent of the  $N_D$  phase confines these anisotropic properties to a range of temperature often not suitable for applications. In order to stabilize anisotropic DLC films, we applied the in-situ photopolymerization process to reactive DLCs.

We will describe the synthesis of various new discotic liquid crystalline acrylates and the influence of the number of acrylate groups (per molecule) on their liquid crystalline phases and on their photopolymerization behavior. We will discuss the influence of the photopolymerization on the thermal stability and on the optical properties of the resulting polymer films. Finally, we will correlate these results with the structural data obtained by X-Ray diffraction analysis.

A2P.09

A NEW CLASS OF NON-SYMMETRICAL METAL-CONTAINING LIQUID CRYSTALS. PERIPHERAL FUNCTIONALISATION AND REACTIVITY.

I. M. SAEZ \*, P. STYRING. School of Chemistry, University of Hull, Hull HU6 7RX, UK.

Peripheral monofunctionalisation is the key feature to unsymmetrical reactive metal complexes, which allows their subsequent incorporation as side chains onto a polymeric backbone [1]. We have designed and synthesised a family of a *new* type of unsymmetrical ligands and metal complexes, which allows the single functionalisation of the metal containing monomer. Complexation to M(II) cations promoted liquid crystalline behaviour in the monomers. The low molar mass metal-containing monomers have been incorporated into oligomeric polysiloxanes through the hydrosilylation reaction of an olefinic double bond under very mild conditions, to produce liquid crystalline metal containing- oligomers free from crosslinking. The effect of a terminal siloxy group on the mesogenic properties of the metal- containing low molar mass mesogen has been studied. Their optical and thermal properties are presented.

[1] L. Oriol, J. L. Serrano, Adv. Mater. 1995, 7, 384. \*Supported by EPSRC Grant GP/ K / 08567.



FERROELECTRIC LIQUID CRYSTALLINE POLYSILOXANES IN WHICH THE CHIRALITY IS INTRODUCED VIA AN ASYMMETRIC SULFUR ATOM.

S.J. Méry, L. Catala, J-F. Nicoud, Y. Galerne, D. Guillon. I.P.C.M.S./G.M.O., C.N.R.S. 23 rue du Loess, BP 20 CR, F-67037 Strasbourg Cédex.

We have synthesized and investigated the properties of two series of ferroelectric liquid crystalline polysiloxanes bearing a chiral n-alkyl arenesulfinate moiety. The synthesis of the materials was possible through 3 successive polymer-analogous reactions. The efficiency of the reactions was such that up to 97% overall substitution rate of the siloxane units of the polymers by the mesogenic moieties could be obtained. The mesomorphic properties as well as the preliminary investigations of the ferroelectric properties of the polymers will be presented. Finally, the effect of the substitution of the sulfur atom by a carbon one will be discussed in comparing the mesomorphic properties of the sulfinate-based polymers and molecules with their carboxylate counterparts.

## A2P.11

LC VINYL MONOMERS AND POLYMERS BASED ON ANILIDES OF FORMYLBENZOYLMETHANES. INTRA- AND INTERMOLECULAR HYDROGEN BOND AND CIS-TRANS ISOMERISM, V.V.Zuev, Institute of Macromolecular compounds of RAS, Bolshoi pr.31, St. Petersburg, 199004, Russia.

For the present investigation we synthesized vinyl derivatives of formylbenzoylmethanes and corresponding polymers. This compounds have cis(C) and trans(T)- isomers. C is stabilized by intramolecular H-bond, whereas the stability of T is ensured by intermolecular H-bond with another molecule of this compounds. The temperature dependence of the C-T ratio was investigated in solid and LC (nematic) state by NMR and IR spectroscopy. In solid and LC state most prefereble is C isomer. Fraction of T isomer is about 1-2% and slightly depends from the temperature. In solid polymers T isomer exist only in amorphous domains.

## A2P.12

SYNTHESIS OF NEW LIQUID CRYSTALLINE COPOLYMERS AND POLYMER BLENDS WITH ELECTRON DONOR AND ACCEPTOR GROUPS, YanQing Tian<sup>1</sup>, YingYing Zhao<sup>1</sup>, XinYi Tang<sup>1</sup>, XiMin Huang<sup>2</sup>, <sup>1</sup> Department of chemistry, Jilin University, Changchun 130023, 2 Changchun Institute of Physics, Chinese academy of Sciences, ChangChun 130022, P.R.C.

A series of Liquid crystalline copolymers between 4-[[6-(acryloxy)hexyl]oxy]-4'-nitroazobenzene (6AzNO2) and 4-[[6-(acryloxy)hexyl]oxy]-benzylidene-4'-(N,N-dimethylamino)aniline(6BDMA) were prepared. The homopolymer of 6AzNO2 was smectic polymer, the homopolymer of 6BDMA was nematic liquid crystal, while all of their copolymers showed broader smectic A phases which were attributed to the interactions between the electron donor and acceptor groups [1]. Smectic A phases were also observed for their binary polymer blends and the binary mixtures of their model compounds.

[1]. Y.Kosaka, and T.Uryu, J.of. Poly. Sci. Poly. Chem. 33, 2221 (1995).

SYNTHESIS OF NOVEL POLYMERIC LIQUID CRYSTALS,

G. Subramaniam, Department of Chemistry, Penn State University, Hazleton, PA
18201, USA.

We are interested in exploring the possibile novel architecture for polymeric liquid crystals; and to achieve it by self-assembly and conventional polymerization reactions. To achieve this end a number of achiral and chiral liquid crystals are being synthesized. A few of the approaches used in the assembly of polymers include acid-base chemistry, metal complexation, hydrogen bonding, incorporation into biopolymers and polyhydrosilylation. A few of the polymeric backbones of interest are polydimethylsiloxane, polydimethylsilozene, polyethylene, polypeptide and polyvinyl alcohol. The poster will discuss the details of our synthetic efforts towards achieving these novel materials.

A2P.14

THE FIRST TWO-RING MESOGENS HAVING A LATERAL AROMATIC BRANCH AND CORRESPONDING POLYSILOXANES, W. Weissflog, and A. Hohmuth, Max-Planck-Research Group Liquid Crystalline Systems, Muehlpforte 1, 06108 Halle, Germany

Synthesis and properties of two-ring mesogens having a phenyl ring within the lateral branch are described (1). The length of the terminal chains is of great importance for the existence of liquid crystalline state as become known by the melting behaviour of two homologous series. Compounds having longer aliphatic groups exhibit nematic and/or smectic A phases in dependence on the type and position of substituents located at the lateral aromatic ring. Surprisingly, the mesophase stability can be higher than for the laterally unsubstituted parent mesogens. Therefore, discussion of the length-to-breadth ratio can not give an explanation for the existence of mesophases of these novel liquid crystals having a nonconventional molecular shape. For the linking such mesogens to polysiloxane three different para-positions were used to serve as starting point of the spacer. Comparing with the low-molecular mesogens interesting changes of the mesophase behaviour are noted depending on the length and the linking position of the spacer. Mesophase stabilization of different scale is found. In some cases the polysiloxanes produced from "non-mesomorphic" monomers show enantiotropic phases.

(1) A. Hohmuth, and W. Weissflog, Liq. Crystals, submitted

A2P.15

BLUE PHASE FORMATION IN LIQUID CRYSTAL POLYMER MIXTURES Upindranath Singh, Physics Department, University of the West Indies, P.O. BOX 64, Bridgetown, BARBADOS

Fred J. Davis, J.J. Thomson Physical Laboratory, Polymer Science Centre, University of Reading, Whiteknights, Reading RG6 2AF, UNITED KINGDOM

Polarized light microscopy was used to investigate blue phase formation in mixtures of the chiral nematic liquid crystal (+)-2-Methylbutyl p-[(p-Methoxybenzylidene)amino]-cinnamate (MBMBAC) and the nematic side chain polymer (cyanophenyl benzoate acrylate monomer copolymerized with 10% of 2-hydroxyethyl acrylate). The phase diagram and textures are compared to the case in which the polymer is replaced by a low molecular weight nematic.



ORIENTATION OF THE BACKBONE STRUCTURE OF POLYIMIDE WITH ALKYL SIDE-CHAINS: DETERMINATION BY INFRARED ABSORPTION SPECTROSCOPY, K. Sakamoto, N. Abe, R. Arafune, and S. Ushioda, Research Institute of Electrical Communication, Tohoku University, Sendai 980-77, Japan

By infrared absorption spectroscopy we have determined the orientation of the backbone structure of polyimide with alkyl side-chains in rubbed films. The backbone orientation was determined from the dichroic ratio at normal incidence and the incident angle dependence of absorption by the C-O-C asymmetric stretching vibration, the C-N stretching vibration of the (OC)<sub>2</sub>NC bond, and the phenyl C-C stretching vibration. All of them are polarized along the backbone direction. We found that the backbone structure is oriented along the rubbing direction and tilted up on average by 23° from the surface. The pretilt angle of bulk liquid crystal (LC) in contact with this rubbed films is 9.6°. In contrast the pretilt angle of bulk LC and the average inclination angle of the backbone for polyimide without a side-chain (PMDA-ODA) are 2.3° and 8.5°, respectively [1]. The polyimide with alkyl side-chains has much higher backbone inclination angle, and causes a greater pretilt angle in LC than the polyimide without a side-chain. We suggest that the high inclination angle of the backbone structure of polyimide with alkyl side-chains plays an important role in causing a high pretilt angle in bulk LC.

[1] K. Sakamoto et al., Jpn. J. Appl. Phys. 33, L1323(1994).

## A2P.17

ORDERING IN THIN FILMS OF HYBRID MESOGENIC BLOCK COPOLYMERS, G. C. L. Wong<sup>1</sup>, J. Commandeur<sup>1</sup>, H. Fischer<sup>2</sup>, and W. H. de Jeu<sup>1</sup>, (1) FOM Institute for Atomic and Molecular Physics, 1098SJ Amsterdam; (2) Dept. of Chemistry, University of Eindhoven, 5600MB Eindhoven, the Netherlands.

For temperatures below the order-disorder transition, molten diblock copolymers can microphase-segregate into bulk phases consisting of layers, cylinders, spheres, or even topologically complex bicontinuous phases. Since the connectivity of the immiscible polymer components prevents macrophase segregation, the system will separate instead into microscopic domains, the size of which is determined by the competition between entropic losses associated with polymer chain stretching, and enthalpic penalties associated with interface formation. Recently, sidechain liquid crystal polymers have been incorporated into such diblock copolymers, where the mesogenic ordering of the side groups can modify normal copolymer ordering. We have investigated the influence of this molecular architecture on the thin film morphology of one such hybrid mesogenic copolymer (PChEMA-PS) on float glass, using a combination of x-ray reflectivity and AFM. Preliminary experiments indicate strong homeotropic anchoring of the mesogenic groups to the substrate and to air. Small changes in the volume fraction of PS can enforce a conformational transition in the wetting layer of the copolymer, so that both homeotropic as well as planar alignments of the copolymer lamellae are possible. Moreover, due to the excluded-volume interaction of the mesogenic groups, significant deviations from the expected N<sup>2/3</sup> stretched chain conformation are found in the PS block.

## A2P.18

SURFACE-INDUCED TRANSITIONS IN POLYMERIC NEMATICS, <u>P. Biscari</u><sup>(1)</sup>, and E. G. Virga<sup>(2)</sup>. <sup>(1)</sup>Dipartimento di Matematica, Politecnico di Milano, MILANO (Italy); <sup>(2)</sup>Dipartimento di Matematica, NAPOLI (Italy).

New polymeric liquid crystals can be treated as standard nematic liquid crystals when only their bulk properties are at issue, but they exhibit peculiar surface properties. The most striking one is the possibility that biaxial distributions be induced on a confining surface. Continuously varying the surface anchoring, we find a first order phase transition from homeotropic to planar alignment in the bulk.

There is precisely one surface biaxial distribution that induces bistability: it depends on the elastic constants in Landau-de Gennes' free energy functional. The analysis of the model we propose can prove useful in detecting the sign of the difference between splay and bend constants.

SWITCHABLE MAIN CHAIN FERROELECTRIC LIQUID CRYSTALLINE POLYMERS, T. Sierra, A. Omenat, J. Barberá, J.L. Serrano, Química Orgánica. Facultad de Ciencias-I.C.M.A. Universidad de Zaragoza-C.S.I.C. 50009-Zaragoza. Spain.

Two chiral main chain liquid crystalline polymers showing ferroelectric switching in the SmC\* phase are reported. Both compounds contain oligooxyethylene spacers with two (Polymer I) or one (Polymer II) L-(-)-lactic acid chiral units. A sequence I-Ch-SmC\*-SmX-g has been deduced for both of them from optical microscopy observations.

Oriented fibers drawn from each molten polymer in the SmC\* state have been studied by means of X-ray diffraction. The diffraction patterns were obtained at room temperature and at the temperature of the SmC\* phase. Room temperature X-ray data indicate well aligned layered structures for both polymers corresponding to the presence of a crystalline phase. This phase has been identified as an orthogonal SmE phase for Polymer I and a tilted SmK phase for Polymer II. The parameters of the SmC\* phase have been determined from X-ray patterns obtained at higher temperature.

A2P.20

INFLUENCE OF POLYMER IN POLYMER LIQUID CRYSTAL GELS, J. Nourry, A. Magnaldo, and P. Sixou, Laboratoire de Physique de Matière Condensée, CNRS URA 190, F-06108 Nice Cedex 2, FRANCE. A. Boudet, M. Mitov, V. Tournier-Lasserve, CEMES LOE/CNRS, BP 4347, F-31055 Toulouse Cedex, FRANCE.

We have investigated gels made by a L.C. polymer and different liquid crystal solvents. Both the mesomorphic polymers and liquid crystals used were either nematic or cholesteric. LCs have positive dielectric anisotropies. The polymer concentrations were between 1 to 20% wt. We examined the polymer influence on the morphologies and the optical characteristics such as direct-direct and direct hemispherical transmitivities, reflectivity or dynamic response. Concerning the chiral LCs blends, we studied the influence of the polymer addition on the main electro optical behaviors of liquid crystals with either the same or opposite chirality as the cholesteric polymer additive. We have observed that for low weight concentrations, the polymer did not really affect the liquid crystal behaviors, but, it stabilized the main cholesteric states. Then, up to a certain threshold polymer concentration, around 15%wt, the effect of the phase separation is discernible. Moreover, the liquid crystal could not be electrically aligned. Parallely, investigations were carried out in order to connect the electro-optical behaviors of the systems with their microscopic morphologies as they are closely linked. Furthermore, we also studied mixtures polymerized in various conditions, such as in the anisotropic or isotropic phase and in the homeotropic state. We analyzed their influences over both the morphologies exhibited and the electro-optical characteristics of these systems.

A2P.21

NMR STUDIES OF DIRECTOR DYNAMICS AND VISCOELASTIC PROPERTIES IN LIQUID CRYSTAL POLYMERS, <u>G. Kothe</u>, M. Tittelbach, N. J. Heaton, C. R. Leal\*, J. B. Ferreira\*, and A. F. Martins\*, Dept. Physical Chemistry, University of Freiburg, Albertstr. 21, Germany, \*Dept. Materials Science, The New University of Lisbon, 2825 Monte de Caparica, Portugal.

In this paper we present the results of deuteron ( $^{2}$ H) NMR studies conducted on nematic liquid crystal polymers. Pulse frequency dependent transverse  $^{2}$ H spin relaxation techniques have been employed to characterize the thermal fluctuations of the director about its equilibrium orientation. Analysis of the dispersion profiles provides values for the bend viscosity and an effective elastic constant of the material [1]. Impulsive rotation of the initially homogeneous nematic sample by an angle of  $\alpha$  =90° in the static magnetic field of the spectrometer creates a non-equilibrium state, which on decaying, leads to the formation of a transient periodic pattern. Analysis of the time-dependent  $^{2}$ H NMR spectra, recorded during the transient process, gives a wealth of information on the director dynamics and on the viscoelastic properties of the liquid crystal polymers. In particular, four out of the five Leslie viscosities and the ratio of two Frank constants are obtained from the analysis [2].

[1] N. Heaton, D. Reimer, and G. Kothe, Chem. Phys. Letters 195, 448 (1992).

[2] M. Tittelbach, G. Kothe, C. R. Leal, J. B. Ferreira, and A. F. Martins, Chem. Phys. Letters 1996, submitted.



MECHANICAL BEHAVIOR OF SIDE-CHAIN LIQUID CRYSTALLINE NETWORKS, L. Hilliou, J.L. Gallani, P. Martinoty, F. Doublet, and M. Mauzac, Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex France.

The mechanical properties of a homologue series of side-chain mesomorphic networks were studied with a piezorheometer over frequencies ranging from  $10^{-2}$  to  $10^4$  Hz. The results [1] show that these networks display original dynamic behavior which is very different from the purely elastic behavior observed with the same conditions on the bare network. Their response is governed essentially by the dynamic glass transition and the critical effects associated with the N-SmA transition only appear as slight anomalies. For each of the samples, the static rigidity modulus  $G_0$ , the infinite-frequency dynamic rigidity modulus  $G_\infty$ , and the characteristic frequencies respectively associated with the largest viscoelastic mode and with the glass transition, were determinated.

[1]J.L. Gallani, L. Hilliou, P. Martinoty, F. Doublet and M. Mauzac, J. Phys. II France 6 (1996) 1-19. \*Centre de recherche Paul Pascal, CNRS, Avenue du Docteur Schweitzer, 33600 Pessac France.

## A2P.23

ELECTROSTATIC FIELD-INDUCED TRANSFORMATION IN THE HOMEOTROPICALLY ALIGNED LIQUID CRYSTALLINE POLYMER, K. Monzen, K. Hiraoka, Y. Uematsu, and M. Date\*, Tokyo Institute of Polytechnics, Atsugi, Japan.

\*The institute of Physical and Chemical Research, Wako, Japan.

Poly( $\gamma$ -benzyl L-glutamate), PBLG having the large dipole along the molecular axis forms generally cholesteric liquid crystal in concentrated solutions and however frequently gives a nematic texture aligned homeotropically at a glass surface. In this report, for the LC solution of PBLG/1,1,2-trichloroethane, the effect of D.C. field applied perpendicularly to the director in a homeotropic texture was investigated by microscopic optical measurements. An increase of the D.C. field above a threshold generates some planar texture at an electrode and the texture develops with a distinct boundary between the homeotropic and the planar ones. After the field direction was inverted, the boundary begins to move backward into an electrode, and at the same time, the planar texture to develop slowly from the another electrode. Under a fixed strength of the field, the ratio of the homeotropic and the planar areas is kept constant after an inversion and the value depends on the field strength. The phenomenon is qualitatively explained by considering the dielectric instabilities associated with some electrostatic interaction between the glass surface and polymer ends.

#### A2P.24

THERMOTROPIC MAIN CHAIN LIQUID CRYSTALLINE POLYMERS WITH LATERALLY ATTACHED MESOGENIC UNITS, J.K. Kallitsis<sup>(a)</sup>, H.S. Serpi<sup>(b)</sup>, C. Tosioudi<sup>(a)</sup>, K.G. Gravalos<sup>(a)</sup>, P.J. Photinos<sup>(c)</sup>, and D.J. Photinos<sup>(b)</sup>, (a) Department of Chemistry, University of Patras, Patras 26500, Greece, (b) Department of Physics, University of Patras, Patras 26500, Greece, (c) Department of Physics, Southern Oregon State College, Ashland, Oregon 97520, USA.

A molecular theory is developed for the study of orientational ordering in a main chain polymers consisting of rodlike mesogenic units attached at an angle to aliphatic spacers. The variation of the linkage angle is found to have rather profound effects on the order parameters and temperatures of transition from the isotropic to the ordered melt as well as on their characteristic odd-even alternations with spacer length. The oblique attachment of the rods at an angle of roughly 60° is predicted to lead to maximal reduction (estimated at 200°C) of the transition temperature relative to the longitudinal attachment. In an attempt to produce compounds of this type we have synthesised a new series of semirigid main chain poly(alkylene-2,5-diphenyl-terephthalate)s with terphenyl mesogenic groups attached laterally to the spacer chain. DSC thermograms and cross polarised optical microscopy textures exhibit typical liquid crystalline behaviour for members of this series with spacers containing more than 8 carbon atoms and this occurs at substantially lower temperatures than in the case of longitudinal attachment.

\* Supported in part by the EC under Human Capital and Mobility Programme contract ERBCHRXCT930161.

#### MECHANICAL SWITCHING AND SOFT ELASTICITY IN LIQUID CRYSTAL ELASTOMERS

PM Roberts, GR Mitchell, FJ Davis, H Hirschmann, JA Pople, PA Keates,

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Liquid crystal elastomers have been produced by cross linking side chain liquid crystal polymers to form stable, free standing films. Monodomain or single crystal elastomers are produced by cross linking the polymer which has been previously oriented in a magnetic field. The introduction of cross links defines the state of lowest energy for the film and leads to interesting phase behaviour including a memory of the state of order at cross linking. The configuration of the backbone couples to the state of order of the mesogens thus when a mechanical field is applied to an unoriented sample order parameters of up to 0.7 are achieved at extensions ratios of 20-30%. More interestingly in a uniform monodomain film there exists the possibility for 'soft' modes. Here if the field is applied perpendicular to the initial director it exhibits a discontinuous rotation to align with the applied field at no cost to the free energy of the sample. The question which arises is to ascertain how 'soft' this mode is. At angles smaller than 90° the reorientation is more continuous. By using magnetic fields to produce the monodomain we have an easy route to the exploration of different deformation geometries, for instance a film can be produced with the director perpendicular to the films surface. The uniformity of the response of the elastomer to the applied field is investigated using optical microscopy and x ray diffraction using an area detector fitted with an x-y stage.

A2P.27

DIELECTRIC PROPERTIES OF NOVEL HOMOPOLYMER, COPOLYMER AND BLENDS OF SIDE CHAIN LIQUID CRYSTAL POLYMERS. George P. Simon <sup>1</sup>, Ronald Chuah <sup>1</sup>, Gary M. Day <sup>2</sup>, W. Roy Jackson <sup>2</sup>, Yu Nagase <sup>3</sup>, Eiichi Akiyama <sup>3</sup>, Yuriko Takamura <sup>3</sup> and Yue Zhou <sup>4</sup>, (1) Materials Engineering and (2) Chemistry, Monash University, Victoria, Australia 3168, (3) Sagami Chemical Research Centre, Nishi-Ohnuma, Sagamihara 229, Japan (4) Department de Chimie, Universite' de Sherbrooke, Quebec, Canada J1K 2R1

Dielectric relaxation spectroscopy (DRS) is a powerful and relevant method for examining the mobility of side chain liquid crystalline polymers (SCLCPs). The application of these materials lies largely in non-linear optic or information storage applications where motion of the mesogen attached to the polymer chain either during alignment or thereafter to maintain stability is crucial. Whilst detailed fundamental and experimental work has been done on particular materials, we present relaxation and alignment results from a range of the varied and rich chemistries possible for SCLCPs. This includes looking at the effect of copolymerisation, blending, formation of SCLCP ionomers and spacer length on relaxation. It is also found that dc conductivity (observed at the low frequency end of the DRS measurement) is sensitive to the structure of the anisotropic phase, as opposed to purely the main-chain motion (as found in isotropic polymers). The ability of these materials to be aligned in ac electric fields in a manner dependent on the frequency of the aligning filed is also exploited in order to understand the way in which the mesogens self-assemble.

A2P.28

MOLECULAR-STATISTICAL THEORY FOR ELASTICITY OF SMECTIC SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS\*, Hua Zhong, Rolfe G. Petschek, Physics Department, Case Western Reserve University, Cleveland, OH, 44106-7079, USA. We study the molecular statistical theory for the elasticity of side-chain liquid crystalline polymers in smectic A phase. When smectic ordering of the pendants is strong, the back bone polymer tends to be confined in a single plane parallel to the smectic layers. For a polymer to hop from one layer to another is expected to require significant free energy and, in many systems, is known to be rather uncommon experimentally. We show that the statistical analysis of the side-chain liquid crystalline polymers can be mapped into a simple band structure problem. Tight-binding theory in the direction of the layer normal implies that for a strong smectic potential the bandwidth is narrow. Using this fact together with perturbation theory and simple symmetry arguments we find that some of the elastic coefficients diverge. We give a set of symmetry based rules to understand qualitatively the behavior of the elastic coefficients in a variety of polymeric systems.

\* Supported by ALCOM and the Ohio Boards of Regents.



INTERMOLECULAR HYDROGEN BONDED LIQUID CRYSTALS, YanQing Tian 1,2, YingYing Zhao 1, XinYi Tang 1, XiMin Huang 2, 1 Department of chemistry, Jilin University, Changchun 130023, P.R.China, 2 Changchun Institute of Physics, Chinese academy of Sciences, ChangChun 130022, P.R.China.

Liquid crystals built through intermolecular hydrogen bonding between polymaleic acid(PMAA), 6-[(4-hexyloxy-4'-biphenyl)oxy]-1-hexyl polymaleicated(PMAN-HBH) and 4-heptyloxybenzoxy-4'-stilbazole(7SZ), 4-hexanoyloxy-4'-stilbazole(6COSZ) were investigated respectively. The results show that the complexes between PMAA and 7SZ exist not only nematic, smectic A phases but also smectic C phases which don't exist in both the proton donor and proton acceptor. While the complexes between PMAA and 6COSZ aren't liquid crystals. The reason will be discussed.

#### A2P.30

STUDIES ON A POLYMERIC LIQUID CRYSTAL AT AIR WATER INTERFACE A. Bhattacharyya and K. A. Suresh, Raman Research Institute, Bangalore 560 080, India

We have carried out surface manometry and epifluorescence microscopic studies on a polymeric liquid crystal (siloxane polymer of 1-methyl propyl 4 (4'-hexyloxybenzoyloxy) benzoate,  $n \sim 40$ ) at the air water interface. In bulk, this compound shows the phase sequence; glass -7°C  $S_C^*$  76°C I. Our surface pressure-area isotherms show that at room temperature, there are four steep regions separated by plateaus indicating structural changes. From epifluorescence studies, we find that the usual liquid-expanded (LE) phase, on compression at room temperature, transforms to a new phase. On further compression this phase changes to a melted stripe phase[1]. At 35°C, on compression, the LE phase changes to another new phase which appears as large uniformly bright domains. On cooling, these domains transform back to the melted stripe phase.

[1] M. Seul and M. J. Sammon, Phys. Rev. Lett. 64, 1903 (1990).

## A2P.31

PECULIARITIES OF LIQUID CRYSTALLINE ORDER FORMATION IN POLYESTERS WITH IRREGULAR CHEMICAL COMPOSITION, <u>A.V. Purkina</u>, B.Z.Volchek, D.A.Medvedeva, S.V. Shilov, institute of Macromolecular Compounds of Russian Academy of Sciences, St. Petersburg, 199004, Russia.

With the aim of determination of both general rules of liquid crystalline (LC) order formation in polymer melts and effect of LC state on conformational and orientational parameters of macromolecules the following types of polymers were investigated. A: RF-polyesters with azobenzene (AZ) unit in R-fragment. Activation energy of trans-to cis transformation in AZ unit under UV radiation in different phase states was estimated. It was shown that LC ordering stabilises more extended trans-form of AZ unit. Effect of conformational transitions in AZ groups and as a result irregular structure of mesogens on characteristics of F-fragments in LC state were also studied. B: aperiodic random RF-copolymers (CPL) with the same R-fragments and various lengths of F-fragments. It was shown that possibility of smectic type LC order formation in such type of CPL is determined by either conformational changes in spacer or "loosening" of smectic layers. Mechanism of LC order formation depends on asymmetry and chemical structure of R-fragment.

MORPHOLOGY AND DEFECTS IN LIQUID-CRYSTALLINE POLYMERS, S. D. Hudson and H. T. Jung, Case Western Reserve U., Cleveland, OH 44106, USA

The molecular organization, orientational and translational defects, and the overall texture of liquid-crystalline polymers were examined by electron microscopy. Electron diffraction, high-resolution and dark-field microscopy were used to determine molecular packing in various liquid crystalline phases formed by semiflexible polymers. This organization was confirmed by the existence of certain defects. Applied forces that align the mesophase influenced the types, population, and clustering of such defects. The type and quality of alignment has been examined as a function of flow conditions.

A2P.33

LIGHTLY CROSSLINKED LIQUID CRYSTALLINE EPOXY RESINS,

M. Giamberini, E. Amendola, C. Carfagna, Department of Materials and Production Engineering, University of Naples "Federico II", Piazzale Tecchio 80, 80125 Napoli, Italy.

Rigid rod epoxy endcapped monomers can be cured in liquid crystalline phase. We discuss the properties of the thermosets cured with aliphatic diacids: the resulting materials have a low crosslinking extent and still exhibit a liquid-crystalline to isotropic transition. The degree of order of these materials and their phase transition temperatures depend on the length of the acid. Due to their relatively low glass transition temperatures (Tg), close to room temperature, these thermosets can be oriented by moderate stretching above Tg; the resulting orientation is subsequently "frozen" by quick cooling the stretched materials to room temperature. The order parameter of the oriented materials resulted quite high.

A2P.34

DEUTERIUM NMR INVESTIGATIONS OF THE TRANSIENT DIRECTOR DISTRIBUTIONS INDUCED BY A MAGNETIC FIELD IN A NEMATIC POLYMER SOLUTION, <u>J.B. Ferreira</u>, J.R. Hughes<sup>\*</sup>, C.R. Leal, G.R. Luckhurst<sup>\*</sup>, A.F. Martins, and S.J. Picken<sup>†</sup>, Dept. Ciência dos Materiais, FCT, Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal; \*Dept. Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom; \*Akzo Research Laboratories, Dept. Physical Chemistry, P.O. Box 9300, 6800 SB Arnhem, The Netherlands.

We have analysed the deuterium N.M.R. spectra of a nematic solution of poly(p-phenylene-terephthalamide) (aramid) in  $D_2SO_4$ , during the reorientation process following a sudden rotation of the (initially homogeneous) sample through an angle  $\alpha$  about an axis perpendicular to the field direction. When  $\alpha > \pi/4$ , the spectra recorded during the reorientation process show two doublets with time dependent intensity: a sharp one with constant splitting and a broad one with time dependent splitting. This is due to the occurrence of a transient distortion pattern of the director field, described by a time dependent, spatially periodic, distribution function. Very good computer simulations of these spectra were obtained using only two Fourier components (1st and 3rd) of the distribution function, coupled with director thermal fluctuations. One single harmonic cannot account for the presence of two intense spectral doublets, the third harmonic being necessary to describe the spectral shape, even at relatively short times after the sample rotation. The simulated spectra were used to evaluate some important viscoelastic parameters of the nematic solution.



THE SYNTHESIS OF SULFUR-CONTAINING SIDE-CHAIN LIQUID CRYSTAL POLYMERS, Weibang ZHANG\*, Lu JIANG, Jiarui XU, Hanmin ZENG, Materials Science Institue, Zhongshan University, Guangzhou 510275, P. R. CHINA.

Thioester-containing liquid crystal possess positive dielectric anisotropy  $(\Delta \varepsilon)$  and excellent physical properties. We have recently synthesized a series of sulfur-containing side-chain liquid crystal polymers, such as poly-4- $(\omega$ -alkyloxyolyl)-thiophenyl 4- $(\omega$ -methacryloyloxy-ethyleneoxy) benzoate. Methacrylate was used as the backbone and the polymers have terminal groups of different lengths. The monomers were identified by <sup>1</sup>H NMR, IR and MS. The polymers were obtained by radical polymerization using BPO as initiator. Results show: (1) While the monomers do not exhibit liquid crystalline properties, their polymers are liquid crystals. (2) The number-average and weight-average molecular weight of the polymers are  $10^4$  and  $10^5$ , respectively. The texture morphology of the polymers exhibits nematic phase. (3) The liquid crystal phase  $(T_i - T_g)$  of the polymers ranges from about  $30^{\circ}$ C to  $60^{\circ}$ C; this range depends on the lengths of the terminal groups. The melting heat  $(\Delta H_i)$  of the polymers is about 1 J/g.

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## A2P.36

THE MECHANISMS OF LIGHT INDUCED ORDERING IN LIQUID CRYSTALLINE POLYMERS, A. Tereshchenko, L. Shansky, G. Puchkovska and O. Yaroshchuk, Institute of Physics, Nat. Acad. Sc., Prosp. Nauki 46, Kyiv 252022 UKRAINE

We present the studies of the light induced ordering in a thin films of azo-dye containing LC polymers [-O-CO-CH(Sp-M)-CO-O-(CH<sub>2</sub>)<sub>8</sub>-], where Sp-M is a side-chain with spacer Sp=-(CH<sub>2</sub>)<sub>6</sub>-O- and azo-dye mesogen M=-Ar-N=N-Ar-NO<sub>2</sub>, by UV- and IR- spectroscopy and photo-induced birefrigence method. The results brought out anisotropic arrangment of azobenzene fragments perpendicular to vector E of the light which leads to the origin of the local anisotropic field. This field causes the partial ordering of polymer macrochains. The time of the arrangment of macrochains is more long that time of the side chains arrangment because of their low molecular mobility. For the exposure times corresponding to arrangment of side chains quazireversible response is observed. Increasing of the exposure time to values corresponding to effective arrangement of macrochains leads to the origin of irreversible recording component followed by the increasing of anisotropy after switching-off of the excited light. A light heating of the samples (upto 50° C) leads to more faster arrangment under the same intensity of the light. Heating of the films above T<sub>c</sub> of LC polymer leads to disappearing of induced ordering.

## A2P.37

THE SYNTHESIS OF SIDE CHAIN LIQUID CRYSTALLINE POLYMETHYLSILOXANE CONTAINING4- (4'-UNDECANOYLOXY) BENZOYLAMINO-BENZO-15-CROWN-5. Chun WU. Qing JIANG. Yong-Chang ZENG and Ming-Gui XIE'. Department of Chemistry. Sichuan University. Chengdu 610064. P. R. China. Liang-Yu WANG. Department of Chemistry. Qinhua University. Beijing. 100084. China

Polysiloxane liquid crystal stationary phase containing crown ether group possesses the chromatographic behaviors of both the side chain liquid crystalline polysiloxane and the side crown ehter polysiloxane (1). The structure of the polymer and its monomer had been verified with IR. MS. <sup>1</sup>HNMR. the nematic mesophase of the polymer were determined by using DSC and Texture. The polymer as stationary phase for capillary gas chromatography was studied. The main chromatographic characteritics. including efficiency polarity and selectivity, were examined and discussied.

[1]R. N. Fu. P. Jing. J. L. Gu. Anal. Chem. 1993. 65(15). 2141.

<sup>\*</sup> Project supported by National Natural Science Fondation of China.

PHYSICAL PROPERTIES OF A SIDE-CHAIN TYPE POLYSILOXANE LIQUID-CRYSTALLINE POLYMER WITH ELECTRORHEOLOGICAL EFFECT, <u>Kozo Tajiri</u>, K. Ohta, M. Sugaya, T. Nagaya, H. Orihara, Y. Ishibashi, M. Doi and A. Inoue\*, Department of Applied Physics, School of Engineering, Nagoya University, Nagoya 464-01, Japan, \* Central Laboratory, Asahi Chemical Industry Co., Ltd., 2-1, Samejima, Fuji. Shizuoka 416, Japan

Recently, it has been found that a side-chain type polysiloxane liquid crystalline polymer (LCP), diluted with dimethylsilicone, shows a large electrorheological (ER) effect[1]. In order to clarify the origin of the ER effect in this system, we investigated the physical properties of pure polymer, not diluted with solvent, by means of X-Ray diffraction, dielectric spectroscopy and electro-optical measurement. As the results it was found that at the room temperature this LCP is in the smectic phase and at 40°C undergoes a phase transition from liquid crystalline to isotropic phase. The dielectric absorption was observed in the frequency range from 10<sup>4</sup> to 10<sup>7</sup>(Hz), which may be due to the relaxation of the mesogenic group motion. In the electro-optical measurement, Kerr-effect with frequency dispersion was observed.

[1] A. Inoue and S. Maniwa, J. Appl. Polym. Sci. 55 (1995) 113.

A2P.39

SYNTHESIS AND OPTICAL CHARACTERIZATION OF CHOLESTERIC POLYMER NETWORKS, Andreas Stohr and Peter Strohriegl, Makromolekulare Chemie I, Universität Bayreuth, D-95440 Bayreuth.

A prominent feature of cholesteric mesophases is the selective reflection of light. If the wavelength of reflection is in the visible range of the spectrum, the phase appears coloured. Thereby the observed color depends on the viewing angle. With increasing angle a blue shift of the reflection color is observed (color flop).

We synthesized densely crosslinked cholesteric polymer networks by in-situ photopolymerization in the cholesteric mesophase. The cholesteric phase is permanently fixed in the networks and stable up to the thermal decomposition. We induced the cholesteric phases by adding chiral compounds to difunctional nematic monomers. As both the pitch of the cholesteric helix and the reflection wavelength strongly depends on the amount of the chiral dopant, this correlation has been carefully elucidated by UV-spectroscopy. We also measured the angular dependence of the reflection wavelength and characterized the networks by colorimetric measurements. Another point of investigation was the influence of solvents on the reflection wavelength.

A2P.40

MEMORY EFFECTS IN MONODOMAIN LIQUID CRYSTAL ELASTOMERS PRODUCED IN MAGNETIC FIELDS PM Roberts, GR Mitchell, FJ Davis,

Polymer Science Centre, Department of Physics, University of Reading, Reading, Berkshire RG6 4AF, England

Magnetic fields have been utilised to produce macroscopically oriented side chain liquid crystal polymer films which were subsequently cross linked to produce monodomain elastomers. The orientation process has been monitored via birefringence, dichroism and x ray scattering techniques and found to be complete in minutes. To introduce the cross linking we have developed a relatively slow, thermally activated cross linking technique which allows for relaxation of the polymer chains before any cross linking has taken place. This cross linking is shown to be complete in around 60 hours via FTIR and gel content measurements. Free standing, stable films are thus produced which show a remarkable memory of the state of order at cross linking even after prolonged annealing in the isotropic phase. On heating such a film through T<sub>NI</sub> a macroscopic shape change is seen as the backbone relaxes back to a random coil configuration. From the size of this shape change we can gain information on the backbone anisotropy and determine interaction parameters between backbone and side chain. We have also set out to explore the results of reducing the effective number of cross links per polymer chain. For samples produced below the gel point there was no longer a memory effect as the backbone could no longer recover its original anisotropic configuration, correlation is given between this value and the theoretical gel point.



PHASE TRANSITIONS AND ORIENTATIONAL ORDER IN SURFACE LAYERS OF POLY-3-FLUORO-ETHYLOXYPHOSPHAZENE, E.I. Riumtsey, A.E.Grishchenko, D.R.Tur, Institute of Physics, St.Petersburg State University, 198904 St.Petersburg, RUSSIA.

By the methods of mechanical and dielectric losses, photoelastisity and by the method of inclined light beam the films of poly-bis-3-fluoro-ethyloxyphosphazene (PFEF) have been investigated. The temperatures of relaxation transitions have been determined: -70° C - glass temperature; +70° C - transition to mesomorphous state and spontaneous disappearence of orientational order in the surface layers; +120° C - transition to mesophase of novel modification, change of molecular fragments packing, decrease of "free" molecular chains number due to forming of a large size mesomorphous regions; +225° C - temperature of isotroping and transition to amorphous state. It was determined that optical segmental anisotripy of PFEF in block twice overcome the same characteristic of PFEF in solution. It is the evidence that a strong orientational molecular correlation accompanied by increasing of thermodynamical rigidity of molecular chains takes place in block in comparison with the molecular rigidity of PFEF in solutions. It was shown that fragments of PFEF molecular chains are located, in general, parallel to films surface. An optically anisotropic surface layers of PFEF have a thickness near 110 µm, that is in 2-3 times thicker then analogous estimation for amorphous carbopolymers. The latter fact means that PFEF has an aptitude for orientational ordering. It has been detected an effect of spontaneous change of orientational order degree in surface layers under thermal treatment of polymer.

A2P.42

CONTRAST MATCHED SANS MEASUREMENTS ON ARAMID SOLUTIONS, <u>S.J. Picken</u>, L. Noirez, G.R. Luckhurst, Akzo Nobel Central Research, Physical Chemistry and Mathematics Department, P.O.Box 9300, 6800 SB Arnhem, The Netherlands

We have performed contrast matched small angle neutron scattering measurements on 11%(w/w) nematic solutions of poly(p-phenylene-terephthal-amide) in sulfuric acid. From this we have derived the parallel and perpendicular radius of gyration in a concentrated nematic solution. Comparing the experimental results for R<sub>g</sub>, respectively 70.3 and 248 Å, to values from molecular statistical models it is found that the chain statistics, in nematic solutions, is governed by the persistence length. The used value of the persistence length, about 300 Å, was determined from measurements on dilute isotropic solutions<sup>1</sup>. Therefore, we conclude that the presence of the nematic order hardly influences the chain statistics and that in such nematic solutions it is likely that the chains will show some hairpin defects. This does not seem to be in agreement with the concept of the deflection length<sup>2</sup> in nematic polymer solutions where the nematic environment acts as a constraint on the polymer statistics.

[1] Q.Ying, B.Chu, Makr.Chem.Rap.Comm., 5, 785 (1984). [2] T.Odijk, Macromolecules, 19, 2313 (1986).

PRETRANSITIONAL BEHAVIOR\*, Jian-feng Li<sup>a</sup>, Karl A. Crandall<sup>a</sup>, Virgil Percec<sup>b</sup>, Rolfe G. Petschek<sup>a</sup>, and Charles Rosenblatt<sup>a,b</sup>, Depts. of Physics<sup>a</sup> and Macromolecular Science<sup>b</sup>, Case Western Reserve University, Cleveland, Ohio 44106 USA

Quasielastic light scattering and ellipsometry have been used to probe nematic fluctuations and nematic wetting at an isotropic liquid crystal -substrate interface in a series of willow-like dendrimer liquid crystals. We find that the pretransitional behavior is qualitatively similar to low molecular weight liquid crystals, exhibiting a Landau-like divergence of the relaxation time and a logarithmic divergence of the optical retardation on approaching the nematic-isotropic phase transition from above. Quantitatively, however, we find that the relaxation times for nematic fluctuations are more rapid than might be expected from large molecules.

Supported by the NSF under grant DMR-9122227

SUPRAMOLECULAR LCPs VIA HYDROGEN BOND ASSOCIATION, C.-M. Lee, C. D. Terrell, A. C. Griffin, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406 USA.

Supramolecular liquid crystalline polymers in which the association chain is held together by hydrogen bond interactions is an area of active interest. While it is readily apparent that linear association does occur in, for example, an AA BB combination of complimentary components; it is a more difficult matter to prove the polymeric nature of the complex. In our system of dicarboxylic acids and bis-pyridyls, it is critical to retard or eliminate crystallization as the complex cools from the isotropic state through the mesophase(s) to ambient temperatures. Crystallization at elevated temperatures from an oligomeric form eliminates the opportunity for polymeric behavior arising at low temperatures from increased effectiveness of the hydrogen bond at holding the association chain together. We have designed and synthesized laterally-substituted diacids which act to retard or eliminate crystallization in these linear complexes leading to classical polymer behavior (glass transitions, fiber formation) in these supramolecular complexes.

This work was supported by the NSF-EPSCoR program.

A2P.45

DIELECTRIC BEHAVIOR IN CHIRAL SMECTIC PHASES OF MAIN-CHAIN POLYESTERS, K. Hiraoka, Y. Sugano, K. Monzen, Y. Uematsu, M. Tokita\*, J. Watanabe\*, Tokyo Institute of Polytechnics, 1583, Iiyama, Atsugi, Kanagawa 243-02, Japan \*Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

We have investigated the SmA-SmC\* phase transition of main-chain polyesters having a mesogenic 4,4'-bibenziate unit by means of dielectric spectroscopy. In the SmC\* phase, a relaxation due to the contribution of the spontaneous polarization was easily observed at several Hz. In addition, we recognized a dielectric relaxation exhibiting softening behavior just above SmA-SmC\* phase transition temperature. The soft mode is usually described as the fluctuation of the molecular tilt angle in the SmA-SmC\* phase transition. The fluctuation of the layer tilt, however, may be responsible for the dielectric relaxation of the soft mode in chiral mesophases of the main-chain polymers, because the monomeric units in neighboring layers are connected together and the fluctuation of the unit's tilt angle is suppressed. We will report the experimental details and discuss the fluctuation models responsible for the dielectric behavior.

A2P.46

INTRINSICALLY BIAXIAL SYSTEMS: A CONTINUUM THEORY FOR ELASTOMERS, P. Biscari, Dipartimento di Matematica, Politecnico di Milano, MILANO (Italy).

Elastomeric networks of polymer liquid crystals are a classical example of "solid liquid crystals". They are organized in aggregates of ellipsoidal shape, which can be represented by a symmetric tensor field L, which is closely related to the nematic order parameter Q. We propose a continuum theory, which tales into account both the mechanical forces that can modify the shape tensor L and the nematic properties of the system. We describe the homogeneous equilibrium configurations of the system, but we also study in some model case the minimizers of the free energy functional bearing spatial distortions.



EQUILIBRIUM STATISTICS OF BRANCHED POLYMERIC LIQUID CRYSTALS, Jonathan J. Stott and Rolfe G. Petschek\*, Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106, USA.

We develop a self-consistent model for the equilibrium statistics of nematic branched polymeric liquid crystals in the mean-field approximation. Both normally and irregularly branched dendrimers are considered. We solved the resulting system of equations numerically to find the nematic-isotropic phase transition. The computed order-disorder transition temperatures scale as a function of the bond continuation probability, or, equivalently as the molecular weight, with an exponent that depends on the intrinsic chemical parameters of the system.

\*Supported by the NSF Materials Research Grant program

## A2P.48

## PHOTOORIENTATION IN LB MULTILAYERS OF THERMOTROPIC POLYMERS

J. Stumpe, Th. Geue, Th. Fischer and H. Menzel, Dept. of Chemistry, Humboldt-University Berlin, Germany

Polymers like 2-hydroxyethyl polyacrylates and "hairy rod" polyglutamates with photochromic azobenzene side groups combine amphiphilic and thermotropic properties. In contrast to the smectic polyacrylates with a flexible backbone, the liquid crystallinity of the polyglutamates is based on stiff polypeptide helices and rod-like side groups. The "hairy rods" are oriented in the dipping in each monolayer. Upon UV irradiation the initial double layer structures of both differently ordered LB systems are irreversibly destroyed due to the E-Z photoisomerization. New ordered structures with modified spacing and in-plane anisotropy are generated by a following VIS irradiation step or annealing. Thus, thermal and photochemically induced order-disorder transitions take place in both systems. Optical anisotropy is induced due to photoorientation in the steady state of the photosomerization on irradiation with linearly polarized light. The photochromic groups were oriented perpendicular to the electric field vector of the incident light. While the layered structure of the polyacrylates is maintained the reorientation process occurs like on a cone. In the LB films of the polyglutamates, however, the nematic-like order of the "hairy rods" backbones strongly influences the reorientation of the side groups in dependence on the spacer length. The dependence of the photo-induced reorientation process on the enthalpic stability of the mesophases, the supramolecular order of the films, the aggregation of the azobenzene moieties and the irradiation conditions will be discussed for both systems.

#### A2P.49

MAIN-CHAIN LCPs AS POTENTIAL AUXETIC MATERIALS, B. Guichard, P.W. Liu and A.C. Griffin, Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406 USA.

Auxetic materials (also known as negative Poisson's ratio materials) are characterized by an expansion in the transverse direction upon stretching. This behavior is rare, but could be of much practical importance. We have designed and synthesized a family of main-chain liquid crystalline polymers which are comprised of both terminally- and laterally-attached rods connected through flexible spacers. The operative concept is that the mesophase field orients the laterally-attached rods in the direction of the other, terminally-attached rods in the quiescent mesophase. However, upon application of a mechanical field (stretching) the site-connectivity of the laterally-attached rods causes them to re-orient perpendicular to the extensional direction leading to an increase in the interchain separation and thereby to auxetic behavior. We will report on the synthetic, characterization and mechanical properties of these polyester LCPs.

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DIRECTOR REORIENTATION OF NEMATIC LIQUID SINGLE CRYSTAL ELASTOMERS (LSCE), H. Finkelmann and I. Kundler, Institut für Makromolekulare Chemie, Universität Freiburg, Sonnenstr. 5, D-79104 Freiburg, Germany

Macroscopically ordered nematic elastomers can be obtained with polymer networks having an anisotropic chain conformation (liquid single crystal elastomers, LSCE). Applying a mechanical field perpendicular to the optical axis of the LSCE causes director reorientation above a threshold stress that resembles the Frederiks transition of low molar mass nematic liquid crystals in the electric field. Interestingly the reorientation process is accompanied with a structure formation within the network. The structure is given by domains that are separated by sharp domain walls. Within the domains the director rotates either clockwise or anti-clockwise towards the direction of the external field. The structure formation may be due to a balance between elasticity of the network and the Frank elasticity of the nematic phase.

A2P.51

X-RAY AND DIELECTRIC STUDIES OF SIDE-CHAIN ORDERING IN POLYMER LIQUID CRYSTALS, Chris Murray\*, D. A. Dunmur\*, G. Ungar\* and M. Verrall\*.\*Centre for Molecular Materials, University of Sheffield, UK. \*Merck Ltd, UK.

This research investigates the molecular packing and dynamics of side-chain liquid crystalline polymers (SCLCPs) using techniques of x-ray diffraction and dielectric relaxation spectroscopy (DRS). Analysis of x-ray diffraction patterns has been carried out for a series of aligned samples of SCLCPs, using a 2D image plate with an on-line scanning facility, interfaced to a Silicon Graphics workstation. The order parameter was obtained from the analysis of the angular intensity distribution of the equatorial arc, the wide-angle scattering. A series of angular intensity profiles for the wide-angle scattering region were analysed for a range of temperatures within the mesophase. Computer fitting of a Maier-Saupe distribution function<sup>1</sup>, gives the order parameters for various temperatures, which are compared with results from the DRS measurements. Dielectric loss and permittivity spectra for the SCLCPs in different alignment states have been produced. These have been used to calculate order parameters using the theory proposed by Attard et al. <sup>2</sup>, which includes director disorder.

[1] LEADBETTER, A. J. and WRIGHTON, P. G., 1979, Journal de Physique, 4, 234

[2] ATTARD, G. S., ARAKI, K. and WILLIAMS, G., 1987, Brit. Polym. J., 19, 119

A2P.52

IN-PLANE SWITCHING IN SPIN-COATED POLYMER LIQUID CRYSTALS: MATERIALS ASPECTS AND APPLICATIONS, K. Skarp, S. Uto\*, M. Ozaki\*, K. Yoshino\*, M. Svensson\*, B. Helgee\*, Department of Physics, \*Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden. \*Department of Electronic Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565, Japan

Preparation of liquid crystal samples with good alignment quality is a basic requirement for nearly all technical applications. The conventional method is to fabricate a sandwich cell with alignment layers. Using a side-chain liquid crystalline polymer with a broad C\*-phase [1], we have developed an alternative method based on spin-coating from solution of a free-surface film [2]. Typically, concentrations of 10 weight-% polymer yield films of 2 µm thickness. The homeotropic orientation is very stable, and electroclinic and ferroelectric switching can be studied directly in the polymer film using in-plane electrodes. Film-switching with electrode distance of 0.5 mm could be achieved in the C\*-phase at surprisingly low fields of about 0.05 V/µm, compared to much higher fields in conventional cells, about 10V/µm. Materials aspects and basic properties of spin-coated films will be described, and a video recording of film structure and electrooptic switching shown. Possible applications of ferroelectric, antiferroelectric, electroclinic and electromechanical effects in spin-coated smectic polymer films will be discussed.

[1] B. Helgee, T. Hjertberg, K. Skarp, G. Andersson, F. Gouda, Liquid Crystals, 18, 871 (1995).

[2] K.Skarp, S.Uto, K.Myojin, H.Moritake, M.Ozaki, K.Yoshino, B.Helgee, Jpn.J.Appl.Phys. 34, 5433 (1995)



SMECTIC TILT ANGLE VARIATION IN A HOMOLOGOUS SERIES OF SIDE-CHAIN POLY-SILOXANES, M. Svensson, B. Helgee, K. Skarp\*, G. Andersson\* and D. Hermann\*, Department of Polymer Technology and \*Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden.

The synthesis of a series of side-chain LC siloxane copolymers is reported, and comparative studies of physical properties of five members of the series were made. The members differ only in the length of the terminal alkyl (going from methyl to hexyl; some results for the propyl was reported in [1]). Measurements of ferroelectricity, relaxation times and electroclinic properties aimed at investigating structure-property relationships for the longer side-chain members. The spontaneous polarization could be measured for three of the members, and was found to be in the 55-130 nC/cm<sup>2</sup> range. It was found that the stability of the chiral smectic C phase decreases with decreasing length of the terminal alkyl ester. The smectic tilt angle in the C phase is nearly constant (35°) for the three longest members. A relationship between electroclinic tilt angles and side-chain-length was found: for longer side-chains the electroclinic coefficient increases markedly. The results are discussed in terms of models for side-chain packing and the dependence of lateral distances of side-chains on the length of the flexible terminal alkyl chain.

[1] M. Svensson, B. Helgee, T. Hjertberg, D. Hermann, K. Skarp, Polym. Bull. 31, 167 (1993).

## A2P.54

PYROPOLYMER BASED ON A PHOTO-CROSSLINKED SmC ELASTOMER, K. Skarp, G. Andersson, R. Zentel\*, M. Brehmer\*, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden, and \*Institut für Organische Chemie, Universität Mainz, JJ. Becherweg 18-20, W-6500 Mainz, Germany.

Organic materials with controlled dipolar order may show interesting piezo- and pyroelectric as well as non-linear optical properties. Examples are PVDF and Langmuir-Blodgett films. In this report, we give results for pyroelectric measurements on a pyropolymer obtained from a photocrosslinkable side-chain polymer. In our case, the polymer is a copolysiloxane with two types of side-chains, one forming the ferroelectric smectic C\* phase, and the other having a photo-crosslinkable terminal group [1]. Crosslinking, with photoinitiator DMPA, was performed at 30°C in the presence of a bias electric field. The resulting elastomer had a smectic C\* phase between 30°C and 52 °C. It was studied in our pyroelectric set-up, where we previously studied a non-crosslinked polymer [2]. The set-up employs the Chynoweth pyroelectric method. The measured pyrocurrent curves reflect the crosslinking process, and also reveal a remanent polarisation in the smectic A phase, originating from sidechain-network interactions. The pyroelectric response shows a marked relaxation after poling the sample with dc-voltage (100 V, 30 seconds).

- [1] M. Brehmer, R. Zentel, G. Wagenblast, K. Siemensmeyer, Macromol.Chem.Phys. 195, 1891 (1994).
- [2] K. Skarp, G. Andersson, R. Zentel, H. Poths, Proc. SPIE, 2408, 33 (1995).

#### A2P.55

PHOTOPOLYMERIZATION IN ORDERED SYSTEMS, L.-C. Chien\*, Mary N. Boyden, Andrew J. Walz, and Ibrahim G. Shenouda, Liquid Crystal Institute, Chemical Physics and NSF ALCOM Center, Kent State University, Kent, OH 44242.

Mesogenic monomers of 4-[6-(acryloyloxy)hexoxy]benzoic acid (AHB) and 4-[[6-[(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoic acid 4'-[(1-oxo-10,12-nonadecadiynyl)-oxy]-[1,1'-biphenyl]-4-yl] ester (MHNB) are prepared for polymerizations in highly ordered smectic and nematic mesophases and liquid crystal solvents. AHB exhibits smectic C and nematic mesophases, whereas MHNB displays the phase sequence of smectic X, C, A and nematic phases. Highest molecular-weight polymers with widest molecular-weight distribution were found for those polymerizations proceeded in highly ordered smectic phase and smectic solvents. Photopolymerizations took place in nematic systems gave narrowest molecular weight distribution polymers compared with those in other systems.

This research was supported in part by the NSF ALCOM Center Grant DMR89-20147.

# SYNTHESIS AND EVALUATION OF NOVEL SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS WITH SINGLE AROMATIC UNIT

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A series of new polyacrylic polymers with a single perfluoroalkyl aromatic unit mesogens have been synthesized. The liquid crystal properties of these polymers have been investigated by polarising optical microscopy and DSC. The results show that (1) these polymers exhibit smectic phases when the spacer (CH<sub>2</sub>) is longer than (CH<sub>2</sub>)<sub>3</sub>; (2) as the spacer increased, the S<sub>A</sub> phase temperatures decreased when the length of perfluoroalkyl chain is fixed; (3) as the perfluoroalkyl chain increased, the S<sub>A</sub> phase temperature increased.

A2P.57

MISCIBILITY PHASE DIAGRAMS OF THE MIXTURES OF SIDE-ON SIDE-CHAIN LIQUID CRYSTALLINE POLYMER AND LOW MOLAR MASS LIQUID CRYSTALS,\* M.-C. Chang, H.-W. Chiu, and <u>T. Kyu</u>, Institute of Polymer Engineering, The University of Akron, Akron, OH 44325, N. Leroux and L.-C. Chien, Liquid Crystal Institute, Kent State University, Kent, OH 44242

Temperature-composition phase diagrams of the mixtures of side-on side-chain liquid crystalline polymer and monomeric liquid crystals E44 and E48 have been established by a cloud point method and optical microscope in order to test with theoretical predictions. The theoretical calculation was performed by combining Flory-Huggins free energy for isotropic mixing and Maier-Saupe free energy for nematic ordering of the nematogens. Two orientational order parameters and two nematic-isotropic transitions of the constituent mesogens are taken into consideration in the calculation. The calculated phase diagrams were found to accord well with the experimental phase diagrams. The predicted phase regions and phase boundaries have been confirmed by optical microscopy.

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A2P.58

ELECTROMECHANICAL EFFECTS OF S<sub>C</sub>\* LIQUID SINGLE CRYSTAL ELASTOMERS (LSCE), H. Finkelmann, and T. Eckert, Institut für Makromolekulare Chemie, Universität Freiburg, Sonnenstr. 5, D-79104 Freiburg, Germany

Macroscopically, uniformly aligned  $S_c^*$ -networks (Liquid Single Crystal Elastomers, LSCE) are realized by a two-step crosslinking procedure of  $S_c^*$ -polymers. In the first reaction step a weak functional gel is synthesized that is loaded with a suitable mechanical field to obtain the uniform alignment of the  $S_c^*$ -phase structure. In the second reaction step the network is additionally crosslinked under load to maintain the anisotropic conformation of the network strands.

The non-centrosymmetric phase structure of the  $S_c^*$ -LSCE is proved by SHG-experiments. By mechanical deformation perpendicular to the director of the mesogenic side groups and the smectic layer normal the piezoelectric modulus  $h_{22}$  and the piezoelectric coefficient  $d_{22}$  are analysed as function of the temperature. Although the material is not optimized with respect to these properties,  $d_{22}$  is in the order of  $d_{11}$  of quartz.



## A2P59

BIAXIALITY PHENOMENON IN MOLECULAR PROPERTIES OF COMB LC POLYMER

WITH LATERAL STRUCTURE: FIRST EVIDENCE <u>Peter Lavrenko<sup>1</sup></u>, Heino Finkelmann<sup>2</sup>, Natalia Yevlampiyeva<sup>3</sup> <sup>1</sup>Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy pr.,31, 199004 St.Petersburg, Russia. <sup>2</sup>Institute fuer Makromoleculare Chemie, Universitaet Freiburg, Stefan-Meier-Strasse 31, 7800 Freiburg, FRG. <sup>3</sup>Institute of Physics, St.Petersburg State University, Petrodvoretz, 198904 St.Petersburg, Russia.

Dynamooptical and electrooptical properties have been investigated in dilute solutions for comb-like LC polymer with mesogenic groups laterally attached by middle point to the macromolecule backbone via flexible spacer. For polymer solution in chloroform, the T-range was found where the Kerr constant K is increasing (in absolute value) with increasing T while the shear optical coefficient [n]/[eta] remains invariable. This reflects the intramolecular parking of the mesogen dipole axes with keeping the same order in mesogen optical axes. Dipole axis of the mesogenic group in the chain of this polymer is known to form a large angle with the optical one. Hence, the result can be explained by change in the mesogen short axes parking with the invariable long axes one. By other words, as evidence for present biaxiality phenomenon in molecular properties of the polymer.

CONFIGURATION TRANSITIONS OF NEMATIC DROPLETS IN PDLC, Zhou Fu-San<sup>1,2</sup>, Ou-Yang Zhong-can<sup>2</sup>, Xu Shou-yi<sup>1</sup>, Gao Hong-jin<sup>1</sup>, Zhang Bai-zhe<sup>1</sup>, and You Shi-ji<sup>1</sup>, <sup>1</sup>Beijin Tsinghua Engineering Research Center of Liquid Crystal Technology, Tsinghua University, Beijing 100084, <sup>2</sup>Institute of Theoretical physics, Academia Sinica, P.O. Box 2735, Beijing 100080, China.

A general equilibrium equation of director configuration of nematic droplets with weak homeotropic anchoring is derived including effects of electric field and saddle-splay elasticity. Numerical simulation shows a variety of the configuration transition; 1) There is a threshold of the ratio of anchoring strength and electric field at which a transition from the axial structure to the bipolar one can occur; 2) On the other hand, the increasing of the ratio can induce a transition from the radial structure to the axial structure. It is show that the saddle-splay term has no significant effect to radial structures and less to axial ones. The optical patterns of droplets with different configurations viewed under polarized optical microscope is also simulated. Our numerical method is different from other previous works and may be useful in more complex boundary conditions.

**B1P.02** 

STABILITY OF DEFECTS: INFLUENCE OF THE DIVERGENCE ELASTIC TERMS T. Ishikawa<sup>1</sup>,O.D. Lavrentovich <sup>1,2</sup> and E.M. Terentjev <sup>3</sup> Chemical Physics Interdisciplinary program and Liquid crystal Institute <sup>1</sup> Kent State University, Kent, OH 44242, Isaac Newton Institute of Mathematical Science <sup>2</sup>, Cambridge, CB 3 0EH, U.K. Cavendish Laboratory <sup>3</sup>, Cambridge, CB 3 0HE, U.K.

Energetic stability of point defects is considered using the Frank-Oseen theory including the divergence elastic terms. For the point defect (hedgehog or monopole), it is shown that the ratio of elastic constants defines a radius a of a disclination ring of 1/2 which substitute the hedgehog. The role of the divergence terms in the stability of defects in hybrid aligned nematic films is also considered.

The work was supported by NSF ALCOM Center Grant DMR-20147.

**B1P.03** 

DEUTERON NMR STUDY OF NEMATIC ORDERING IN POROUS GLASSES, A. Zidanšek<sup>1\*</sup>, E. A. Dratz<sup>2</sup>, S. Kralj<sup>3</sup>, G. Lahajnar<sup>3</sup>, M. M. Pintar<sup>3</sup>, and R. Blinc<sup>3</sup>, <sup>1</sup>Department of Physics, Montana State University, Bozeman, MT, USA; <sup>2</sup>Department of Chemistry, Montana State University, Bozeman, MT, USA; <sup>3</sup>J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.

Deuteron NMR lineshape study of the pentylcyanobiphenyl (5CB) liquid crystal confined to the controlled pore glass (CPG) matrices of pore diameters 7, 24, 50, 100, 140, 300 and 400 nm was performed. The nematic to isotropic (N-I) transition is gradual in small pores and discontinuous in large pores. In the nematic phase of small pore samples the absorption spectrum is substantially narrowed, and the N-I transition temperature is decreased. The external magnetic field influence is negligible. The onset of nematic ordering is bulk like in the 300 nm and 400 nm samples, where the absorption spectrum is strongly affected by the external magnetic field. Experimental data can be reproduced using Landau-de Gennes phenomenological approach.

\*On leave from J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia; supported by IIE Fulbright. Program no. 33917 and Slovenska znanstvena fundacija

LIQUID CRYSTAL FORMULATIONS, <u>D.M.G. Agra</u>, F. Amos, L. Davila, M.C. Micaller, L.Cada\* and Z.B. Domingo, Liquid Crystals Laboratory, National Institute of Physics, \*Institute of Chemistry, University of the Philippines, Diliman, 1101 Quezon City, Philippines.

Chiral-Nematic Dispersions and Encapsulation were investigated for the different mixture concentrations of the nematic liquid crystals E7 and E48 and the cholesteric liquid crystals TM74A and TM75A in the Infrared and Visible regime. Liquid crystal (E7:TM74A) dispersions as stand alone systems and as polymer dispersed materials were found to be bistable in the near IR region<sup>1</sup>. Chiral-nematic dispersion of E48:TM74A displayed different bright colors in the 400-760 visible range and exhibited thermochromic properties at room temperature. The PVA encapsulated E48:TM74A mixture (60:40) also showed thermochromicity between 30°C to 43°C. A ternary system was formulated from TM74A:TM75A:E48. Mixtures with high cholesteric concentration exhibited thermochromicity whereas systems with low cholesteric concentration possess electro-optic properties. Gel dispersion was done on mixtures with low cholesteric concentration using a liquid crystal polymer cinnamate. The polymer network effected stabilization on the liquid crystal molecules. Electro-optic tests showed that threshold voltage increases as the cholesteric amount increases in the different LC mixtures. Polymer and gel dispersions also increased the threshold voltages.

[1] Initial results obtained at the LCI-KSU, June 1993.

## B1P.05

A TRENCH TYPE LCD, K. Sano, K. Asakawa, N. Ozawa, T. I. Urano, and S. Machida, Materials and Devices Research Laboratories, R&D Center, Toshiba Corporation, 1 Komukai-toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

For PDLC, PNLC, and PSCT, we propose here a TRENCH TYPE LCD to provide a reflection type LCD capable of operating at low voltage and obtaining an paper white quality of display. The TRENCH TYPE LCD has comb shaped-wall electrodes formed on each pixel, and it contains liquid crystals and polymers in the trench. The depth of the trench is from 20 to 40  $\mu$  m(view direction), and the interval of the wall is from 10 to 20  $\mu$  m. The wall has 5  $\mu$  m thickness. The TRENCH electrode can make the driving voltage low enough as well as the long optical distance.

**B1P.06** 

KINETICS OF PHASE SEPARATION IN MIXTURES OF POLYMERS AND LIQUID CRYSTALS, A. Golemme, A. Urso, B.C. De Simone, G. Chidichimo, S. Zagami#, A. Mashin\*, Dipartimento di Chimica, #Dipartimento di Meccanica, Università della Calabria, 87030 Rende - Italy,\*Dept of Physics, Nizhni Novgorod University, Nizhni Novgorod - Russia

We have used light scattering to study phase separation kinetics in mixtures of liquid crystals and polimerizing materials. We performed experiments at different temperatures and for different liquid crystal compositions. Results show that the kinetic mechanism changes with mesophase content. At higher concentrations we observe kinetics that are qualitatively in agreement with the existing theories describing spinodal decomposition. At lower concentrations the mechanism is different, although the final physical properties of the materials are independent of the decomposition mechanism. We also analyzed our data considering the scaling behaviour expected for the intermediate and late stages of phase separation in polymeric mixtures. Samples obtained in a narrow concentration range where the two kinetic mechanisms overlap, exhibit peculiar physical properties.

NEMATIC LIQUID CRYSTAL-ACRYLATE POLYMER COMPOSITE MATERIAL: PREPARATION, PHASE BEHAVIOR AND ELECTRO-OPTICAL CHARACTERIZATION, E. Roussel<sup>§</sup>, J.M. Buisine<sup>§</sup>, U. Maschke<sup>#</sup>, and X. Coqueret<sup>#</sup>; <sup>§</sup>Equipe de Thermophysique de la Matière Condensée, Laboratoire de Dynamique et Structure des Matériaux Moléculaires, URA CNRS 801, Université du Littoral, Quai Freycinet 1, BP 5526, 59379 Dunkerque, FRANCE; <sup>#</sup>Laboratoire de Chimie Macromoléculaire, URA CNRS 351, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, FRANCE.

New polymer-dispersed liquid crystals (PDLC) materials were prepared by a Polymerization Induced Phase Separation (PIPS) mechanism using U.V. radiation. The samples were obtained from the liquid crystalline components E7 and a mixture of monofunctional (2-Ethyl-Hexyl-Acrylate) and difunctional (1,6-Hexane-Diol-DiAcrylate) monomers as precursors of the matrix.

The thermodynamic properties of both cured and uncured samples were studied by Differential Scanning Calorimetry and optical microscopy. The kinetics of phase separation of PDLC films were examined in the early stages after U.V. exposure. Their optical transmission has been investigated as a function of frequency and amplitude of the applied voltage for several film thicknesses. A high transmission in the ON state and a small memory effect were observed. All results were reproducible within a good accuracy.

B1P.08

ANOMALOUS ELECTRO-OPTICAL RESPONSE OF NCAP-TYPE NEMATIC/POLY-MER DISPERSIONS, O. A. Aphonin, <u>V. F. Nazvanov</u>, Department of Physics, University of Saratov, Astrakhanskaya 83, Saratov 410071, Russia.

We have experimentally investigated the mechanism of switching a composite film consisted of a dispersion of micron-sized nematic (5CB) droplets in a polyvinyl alcohol matrix. Principal transmittances of the film,  $t_{\parallel}$ ,  $t_{\perp}$ , and the phase shift,  $\delta$ , between  $\parallel$  - and  $\perp$  - components were measured ellipsometrically as functions of applied field, E, over the incidence angle range from  $0^{\circ}$  to 75°. It is found that at normal incidence the transmittance curves often exhibit a deep local minimum which can be a 10 times smaller than zero-field transmittance. With increasing the incidence angle, the dependence  $t_{\parallel}(E)$  becomes more complicated acquiring one or two maxima at low fields. At the same time, the dependence  $t_{\perp}(E)$  goes monotone, obtaining the usual S-shape. The  $\delta(E)$  curve is also characterized by anomalous local maximum the position of which well correlates with the minimum in normal transmission curve. These results are discussed in terms of the empirical model which takes into account the non-uniform realignment of the local director in the bulk of nematic droplets and the surface orientation effects at LC/polymer interface.

B1P.09

LINEAR DICHROISM AND BIREFRINGENCE OF NEMATIC/POLYMER DISPERSIONS, O. A. Aphonin, V. F. Nazvanov, Department of Physics, University of Saratov, Astra-khanskaya 83, Saratov 410071, Russia.

A systematic theoretical study is presented of field-controlled light transmission, linear dichroism and birefringence in partially ordered dispersions of nematic droplets with the bipolar director structure in a polymer matrix. The proposed theory considers the orientation-induced changes in the principle turbidities,  $\tau_{\parallel}, \tau_{\perp}$ , and phase shift,  $\delta$ , of a system of single scattering droplets in anomalous diffraction regime. The interference and multiple scattering processes are ignored. In the frame of proposed unified approach, four basic model systems are examined: PDLC and NCAP films in electric (or magnetic) field, PDLC and NCAP films under uniaxial mechanical deformation. The calculated dependencies of  $\tau_{\parallel}, \tau_{\perp}$ , and  $\delta$  on the angle of incidence of probing light, droplet size and shape, refractive indices of LC and polymer, matrix anisotropy, light wavelength, and parameters of external field are presented and discussed in detail. These results are then compared with experiment and used to formulate the criteria for optimization of PDLC and NCAP films for a specific application.

## B1P

#### B1P.10

FRIEDERICKSZ TRANSITION IN ELONGATED NEMATIC DROPLETS, V. V. Presnyakov, S.L.Smorgon, V.F.Shabanov, V.Ya.Zyryanov, L.V.Kirensky Institute of Physics, Krasnoyarsk, 660036, Russia

We have studied the process of reorientation of 5CB nematic droplets dispersed in a stretched polyvinylbutyral film. Unlike [1,2], poles of bipolar droplets have been observed to remain fixed. Reorientation starts at the centre of the droplet gradually progressing towards the droplet surface. It has been found that in samples containing large droplets, the light transmission dependence on the applied voltage has an oscillating behaviour. A qualitative explanation to this phenomenon can be given by using the anomal diffraction approach presented in [3]. An experimental technique is described to determine the Friedericksz threshold value in polymer dispersed nematic liquid crystals. The Friedericksz threshold value has been measured versus the size and the shape of the nematic droplets. The results obtained are analysed in terms of theoretical models [1,2].

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## **B1P.11**

PERMANENT GRATINGS IN PDLC, G. Cipparrone, A. Mazzulla, and F. Simoni§, Department of Physics, University of Calabria, 87036 Rende (CS) Italy. (§) Department of Sciences of Materials and of the Earth, Ancona University, Via delle Brecce Bianche, 60131 Ancona Italy.

We have produced permanent gratings [1] in polymer dispersed liquid crystals by means of an holographic technique which exploit the effect due to the intensity grating created by two Argon Ion laser beams interfering on a PDLC layer. The light intensity modulation originate a material properties modulation. At low light intensity dynamics gratings have been observed [2] while above a certain threshold this material properties modulation remain, even after the induced beams are removed, pointing out the permanent grating formation. These structures are produced by few seconds light exposure, the diffraction efficiency being measured using an He-Ne probe beam. The grating can be erased and rewrited by the same pump beam; moreover, the diffraction efficiency, which shows an anisotropic behavior, can be modulated applying an external AC low voltage field. From preliminary observations the build up of these permanent gratings arise from a combination of thermal and stress effects.

- [1] R. L. Sutherland, V. P. Tondiglia, and L. V. Natarajan, Appl. Phys. Lett. 64, 1074 (1994).
- [2] F. Simoni, G. Cipparrone, D. Duca, and I. C. Khoo, Optics Letters, 16, 360 (1991).

## B1P.12

MONITORING OF PHOTOPOLYMERIZATION THROUGH DIELECTRIC SPECTROSCOPY, D. E. Schuele\*, D. Coleman, and R. Renner, Department of Physics, CWRU, Cleveland, OH 44124, USA

In polymer stabilized liquid crystal cells the monomer content is of order of a few percent. Changes in the cells dielectric properties are monitored during UV radiation. Data will be presented for a PSCT window containing 88.4% E48, 8.4% CB15, and 2.8%DSM monomer with photoinitiator by weight. During polymerization the cells capacitance decreases by 1% and after an initial rise the dielectric loss falls by 40%. Polymerization studies as a function of UV intensity will be presented. Results indicate that the dielectric monitoring serves as an excellent indicator of the polymerization process.

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DIELECTRIC PROPERTIES OF GLASS DISPERSED LIQUID CRYSTALS, <u>J.M.S. Pena<sup>1</sup></u>, E. Olías<sup>1</sup>, X. Quintana<sup>2</sup>, and J.M. Otón<sup>2</sup>. (1)Área Tecnología Electrónica, Universidad Carlos III, Butarque 15, 28911 Leganés, Madrid; (2)Dept. Tecnología Fotónica, ETSI Telecomunicación, Ciudad Universitaria, 28040 Madrid, Spain.

Liquid crystals can be dispersed in gel-glass silica matrices by sol-gel processes. The resulting gel-glass dispersed liquid crystals (GDLCs) are similar to polymer-dispersed liquid crystals; however, the use of an inorganic silica matrix yields a material with enhanced optical and mechanical properties. Dielectric properties of these materials are highly dependent on the manufacturing conditions. Impedance spectroscopy of the isolated silica matrix and the GDLC composite has been employed to characterize the system between 200 mHz and 8 MHz. The results have been compared to theoretical results based on several equivalent circuits. From the optical point of view, GDLCs behave as electrically-controlled wavelength-dependent scatterers [1]. Results derived from dielectric data have been related to the behavior of GDLC optical switches.

[1] J.M. Otón, J.M.S. Pena, A. Serrano, and D. Levy, Appl. Phys. Lett. **66** (8) 929 (1995). Supported by CICyT grant TIC96-0825-C03-01.

**B1P.15** 

UP TO DATE SIMULATION OF LIQUID CRYSTAL DISPLAYS WITH HIGH BRIGHTNESS AND IMPROVED VIEWING ANGLES.

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The simulation of LCDs with the universal modeling system enables us to propose certain new display configurations with high brightness, efficient color reproduction and wide viewing angles. Our success was provided by using special phase retarders, including biaxial phase compensation films and double-cell construction in order to compensate the total phase difference of the LCD. The developed simulation software allows to test an arbitrary director alignment in the cell, including hybrid orientation and nonsymmetric boundary tilt configuration with chiral dopants. The LCDs were simulated both in transmissive and reflective mode, taking into account the properties of metal reflectors, usually used for the purpose. The following new LCD constructions were discussed.

- 1. Birefringent color STN and TN-LCDs with phase retarders without application of isotropic dye filters.
- 2. TSTN projection color systems with improved brightness and efficient color reproduction.
- 3. LCDs based on application of phase retarders, including double cell configurations with improved contrast and wide viewing angles. Our experience shows, that the universal modeling systems proves to be very efficient for preliminary characterization and estimation of new LCD constructions.

**B1P.16** 

INVESTIGATION OF MORPHOLOGY, ELECTRIC AND ELECTRO-OPTICAL PROPERTIES OF A UV-CUREABLE PDLC, Fiore Pasquale Nicoletta\*, Cinzia Caruso\*, Hassan-alì Hakemi+, Michele Santangelo+ and Giuseppe Chidichimo\*, \*Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy; +SNIA-Ricerche, Via Pomarico, 75010 Pisticci Scalo (Mt), Italy.

The results arising from a systematic analysis carried out on morphology, electric and electrooptical properties of a UV-cureable PDLC system are reported. The measurements took place over the liquid crystal concentration range of 0-90%. Such an investigation elucidates the contribution of both the polymer and the liquid crystal in the mechanism of phase separation and allows us to determine correlations between these properties.



A MODEL OF A POWERED NEMATIC DROPLET FOR SMALL ANGLE LIGHT SCATTERING STUDY, Ziqiang Huang\*, Giuseppe Chidichimo, Bruna Clara De Simone, Fiore Pasquale Nicoletta and Cinzia Caruso, Physical Chemistry Laboratory, Dept. of Chemistry, University of Calabria, 87030 Rende (CS), Italy

A powered nematic droplet in axial configuration is modelled as a hollow spheric scatterer for studying its small angle light scattering characters. The term "hollow" means that the central part of the droplet, where nematic molecules are aligned parallel to the incident light, does not contribute scattering intensity; while the shell part where the nematic molecules are supposed to remain in the radial configuration is the effective part of the scatterer. When thickness of the shell is reduced by the external field, calculations by anomalous diffraction (AD) approximation suggest that scattering intensity would decrease and scattering peak would drift to smaller angle. Experiments proved the prediction. Measured angular scattering intensities show good agreement with calculations. As the shell part originates from anchoring of the nematic molecule to the surrounding medium, angular scattering intensity is associated to correlation length by this model.

\* On leave from: Dept. of Opto-Electronic Tech., Univer. of Electronic Scien. & Techn. of China.

## **B1P.18**

ON THE ONSET OF PHASE SEPARATION IN PDLC FILMS, Fiore Pasquale Nicoletta\*, Cinzia Caruso\*, Hassan-alì Hakemi<sup>+</sup>, Michele Santangelo<sup>+</sup> a n.d. Giuseppe Chidichimo\*, \*Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy; +SNIA-Ricerche, Via Pomarico, 75010 Pisticci Scalo (Mt), Italy.

We studied the electro-optics and morpholgy of PDLC films in the concentration range where the microdroplet nucleation takes place. The relationships between the electro-optic properties and morphology of the PDLC are reported.

## B1P.19

ELECTRO-OPTICAL STUDIES OF PDLC TYPE CELLS BASED ON HYDROXYPROPYLCELLULOSE ELASTOMERS, M.H.Godinho<sup>1</sup>, A.F.Martins<sup>1</sup> and J.L.Figueirinhas<sup>2</sup>, <sup>1</sup>Depart. de Ciência dos Materiais and CENIMAT, F.C.T., U. N.L., 2825 Monte de Caparica, Portugal. <sup>2</sup>CFMC, Av. Prof. Gama Pinto 2, 1699 Lisboa Codex, Portugal, and IST, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal.

Very recently a new type of PDLC optical cell based on a cellulose derivative film was proposed.[1] This type of cell is composed of a porous elastomeric solid film impregnated by a nematic liquid crystal and placed between two transparent conducting substrates. The solid films (18-30µm thick) were cast from liquid solutions of the cellulose derivative hydroxypropylcellulose (HPC) with a nominal molecular weight of 100000 in ethanol and acetone, cross-linked with the diisocyanate 1, 4-diisocyanatobutane (BDI). The electro-optical behavior of several of these cells was characterized by light transmission for different preparation conditions that include variation in the number of film layers, in the liquid crystalline layer thickness and in the rugosity of the film surface. The results obtained show that these systems exhibit high transmission coefficients in the on state and that the cells' optical response is very strongly dependent on the number of film layers and on the films' surface rugosity. A preliminary interpretation of these results will be presented and discussed.

[1].M.H.Godinho, A.F.Martins and J.L.Figueirinhas, Liquid Crystals, 1996 (accepted for publication) Support by JNICT, Portugal, under contracts PBIC/C/CTM/1400-92 and PBIC/C/CTM/1411-92.

CORRELATION OF ELECTROOPTICAL AND RAMAN CHARACTERISTICS OF POLYMER-STABILIZED CHOLESTERIC TEXTURE FILMS, Andy Y.-G. Fuh\*, Department of Physics,, National Cheng-Kung University, Tainan 701, Taiwan, ROC; J.-W. Doane, O.-K. Yang, L.-C. Chien, Chemical Physics and Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA; X.-J. Gu, Ontaric Laser and Lightwave Centre, 60 St. George St., Toronto, Ont. Canada M5S 1A7.

We have measured of the Raman and the electrooptical characteristics of Polymer-Stabilized Cholesteric Texture (PSCT) films fabricated with various polymer concentrations. Correlations between these two characteristics were found. This indicates that the Ranman experiment provides us another technique to analyze the PSCT films. The details are reported.

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**B1P.21** 

MEMORY EFFECT AND THE ELECTRIC FIELD IN UNPOWERED NEMATIC DROPLETS, Giovanni De Filpo, Ziqiang Huang\*, Giuseppe Chidichimo and Daniela Imbardelli, Lab. of Physical Chemistry, Dept. of Chemistry, University of Calabria, 87030 Rende (CS), Italy.

Memory effect has been induced by charging PDLCs in strong electrostatic fields for some minutes. The memory time varies from hours to one week strongly depending on the temperature at which PDLC was charged. When PDLC film in memory state are driven by sinuous voltage, it show much more transmission in one half period of the sinuous voltage than in the other half. The effect is explained in terms of internal static field. The electrostatic field in the droplets can be evaluated by measuring the DC bias superposed on the driving voltage to make equal transmission in both half periods of the sinuous driving voltage.

\* On leave from: Dept. of Opto-Electronic Tech., Univer. of Electronic Scien. & Techn. of China.

**B1P.22** 

SIMULATION ON THE KINETIC PROCESS IN POLYMER-DISPERSED LIQUID CRYSTALS: EFFECTS OF VARIOUS CONCENTRATION OF LIQUID CRYSTALS, <u>Shu-Hsia Chen</u> and Wei-Jou Chen, Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, 300, R.O.C.

We developed a dynamical model for the formation in polymer-dispersed liquid crystals[1]. The model has the key feature that the mechanism of polymerization obeys the radical addition polymerization and the movement of molecules is allowed by Kawasaki dynamics. Monte Carlo computer simulations on this model show that the time evolutions of the structure factors exhibits dynamical self-similarity and the mean cluster size of liquid crystals has a peaking behavior until the phase separation is pinned[2]. In the study, the simulation was performed with various concentration of liquid crystals. The mean cluster size of liquid crystal increases as the concentration of liquid crystals increases. We found a relation between the mean cluster size and the concentration of liquid crystals. The simulation results are well consistent with recent experimental observations.

- [1] Wei-Jou Chen and Shu-Hsia Chen, Phys. Rev. E52, 5696 (1995).
- [2] Shu-Hsia Chen and Wei-Jou Chen, Physica A, 221, 216 (1995).

REFLECTION HOLOGRAMS FORMED IN-SITU USING POLYMER L. V. Natarajan\*, R. L. Sutherland, V. DISPERSED LIQUID CRYSTALS, Applications International Tondiglia, and T. J. Bunning, Science Corporation, 101 Woodman Drive, Dayton, OH 45431, USA.

We have recorded reflection grating holograms in polymer dispersed liquid crystalline materials. The gratings recorded with Argon ion laser lines 488 and 514 nm showed high efficiency. The *in-situ*, one step process of making reflection holograms results in periodic layers of polymer and LC-rich planes thin films of lying parallel to the film surface. Electron micrograph study of the gratings show liquid crystal droplets of the order of <100 nm. Very little coalescence of the individual droplets was seen. The grating spacing measured from electron micrographs nearly corresponds to the expected spacing from the observed reflection notch. The electrical switching of the reflection gratings was also investigated.

#### **B1P.24**

IN SITU DIFFUSION AND MISCIBILITY STUDIES OF PDLC SYSTEMS BY FTIR MICROSPECTROSCOPY, Sudarsana R. Challa, Shi-Qing Wang and Jack L. Koenig\*, Department of Macromolecular Science, Case Western Reserve University Cleveland, OH, 44106, USA.

Infrared microspectroscopy was used to study the interaction of liquid crystal(E7) with poly(n-butyl methacrylate) (PBMA). A novel experimental technique is introduced to conduct in situ diffusion and miscibility studies of PDLC systems. The amount of liquid crystal dissolved in the polymer matrix is determined by using the IR microspectroscope which is a powerful tool for characterizing domains on the order of tens of microns. Quantitative phase diagrams are constructed for the PBMA and E7 mixture. It is observed that the diffusion of E7 into PBMA follows Fick's second law of diffusion with a diffusion coefficient of (1.3  $\pm$  0.2) x  $10^{-7}$  cm<sup>2</sup>/sec at 61°C. The intensities of the peaks in the IR spectrum were used as a measure of the concentration of the components. The combination of IR microspectroscopy with the contact method is proven to be a powerful technique for the quantitative elucidation of phase diagrams.

\*Supported by NSF Grant DMR 89-20147

#### **B1P.25**

ELECTRO-OPTICAL STUDIES OF POLYMER DISPERSED LIQUID CRYSTAL FILMS PREPARED BY ELECTRON BEAM PROCESSING, U. Maschke, X. Coqueret, Laboratoire de Chimie Macromoléculaire, CNRS (URA N° 351), Université de Lille 1, F-59655 Villeneuve d'Ascq, France

Polymer dispersed liquid crystal (PDLC) films can be switched electrically from a light scattering offstate to a highly transparent on-state. Polymerization induced phase separation (PIPS) initiated by Electron Beam (EB) radiation has been proved to be a powerful method to obtain defined PDLC films [1]. Compared with the PIPS process by UV light, EB curing results in completely crosslinked polymer matrices without the use of any initiating compounds. An eutectic nematic mixture of cyanoparaphenylene derivatives (E7, Merck Ltd ) was used as liquid crystal material in this work. Blends of an aromatic polyester acrylate in additional monomers were prepared as polymer matrix precursors. Mixtures including different amounts of these materials were submitted to a dose of 60 kGy under an inert atmosphere (Electro-Curtain CB 150). The electro-optical properties of the obtained PDLC-films were investigated as a function of composition, film thickness and driving frequency. The transmission versus voltage curves exhibit a good reproducibility and a strong dependence on the sample composition. The results are discussed in terms of contrast, threshold- and saturation-voltage.

[1] U. Maschke, X. Coqueret, C. Loucheux, J. Appl. Polym. Sci. 56, 1547 (1995).

POLYMER TEXTURES IN THE VICINITY OF LC-DROPLETS IN PDLC FILMS WITH PVA-MATRIX, Yu.V.Panina, V.I.Klenin, D.A.Yakovlev, Chemistry Department, Saratov State University, Saratov, 410071, Russia

We have found experimentally that in polyvinyl alcohol (PVA) films with dispersed LC, manufactured by evaporation of solvent from emulsion of LC in an aqueous solution of PVA at a temperature within mesophase temperature range, supermolecular structure (SMS) of polymer in the vicinity of LC-droplets is oriented (consequently, boundary conditions for LC in the droplets are non-degenerate) and depends on director field configuration in the droplets. The fact is attested by the results of comparison of degree of deformation of supramicrometer-size droplets of nematic (SZK-1) and nemato-cholesteric (SZK-1+1.1%HDN-1) after special heat treatment of the films, leading to uniaxial orientation of polymer matrix [1]. This phenomenon may be explained by assumption that during the process of the formation of SMS of polymer the LC-droplets play the role of anisotropic seeds with the director lines defining preferable directions of the orientation of polymer chains at the droplet surface.

[1] Yu.V.Panina, D.A.Yakovlev, Abst.15 Int.Liq.Cryst.Conf.,1994, Budapest, Hungary, V.1, P.450.

B1P.27

MULTIPLE LIGHT SCATTERING FROM POLYMER-DISPERSED-LIQUID-CRYSTAL MATERIAL; EXPERIMENT AND SIMULATION, <u>Henk M.J. Boots</u>, Jaap H.M. Neijzen, Frank A.M.A. Paulissen, Martin B. van der Mark, and Hugo J. Cornelissen, Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

The angular distribution of light scattered from Polymer Dispersed Liquid Crystal (PDLC) material in the scattering state has been measured as a function of cell thickness. Most cells of practical interest are such that neither a single-scattering nor a diffusion model applies. It is shown that both the angular and the thickness dependence of the scattering intensity are well described by a Monte Carlo simulation of multiple scattering, if in each scattering event the angular distribution is a Lorentzian or a Mie function. Gaussian, exponential, and Henyey-Greenstein distributions fail in this respect. The model smoothly interpolates between the limits for very thin and very thick cells. It can easily be extended to include any specific feature of a scattering display system.

B1P.28

PHOTOPOLYMERIZATION OF PDLC FILMS IN MICROGRAVITY, J.B. Whitehead, Jr.\*, M.M. Chandler and L. Mathias, Depts. of Physics & Astronomy and Chemistry & Biochemistry, The University of Southern Mississippi, Hattiesburg, MS 39406

Polymer Dispersed Liquid Crystal films were photopolymerized aboard NASA's KC-135 aircraft. The PDLC samples were of two prepolymer/liquid crystal systems. The first, an acrylate based prepolymer, SAM114, and the liquid crystal BLO38 and the second, a thiol-ene based prepolymer, NOA65, and the liquid crystal E7. The 10 micron thick PDLC samples were exposed to UV radiation during the 25 seconds of microgravity. The microgravity and the terrestrially produced control films were characterized using electrooptic analysis, optical and scanning electron microscopies, and thermal analysis. The turn-on, turn-off, T<sub>NI</sub>, and sample morphologies of the microgravity samples are compared to the terrestrial control samples. Preliminary results reveal differences in the turn-on and turn-off times of the microgravity and terrestrial samples. SEM analysis revealed the typical "Swiss cheese" morphology for the terrestrially produced 60% E7 in NOA65 and a membrane-like polymer structure was present for the same sample composition photopolymerized in microgravity.

<sup>\*</sup>Supported by NASA Grant NAG13-28, Marshall Space Flight Center and Stennis Space Center



EFFECTIVE MEDIUM THEORIES OF DIELECTRIC PROPERTIES IN PDLC FILMS, V.Yu. Reshetnyak\* and T.J. Sluckin†, Dept. of Mathematics, University of Southampton, Southampton SO17 1BJ, UK.

We have investigated the dielectric properties of PDLC films using effective medium theories of the Maxwell-Garnett family. PDLC films present interesting features because the liquid crystal component exhibits field dependent response, and because the effective medium is anisotropic. The theory is self-consistent and goes beyond previous considerations [1]. The inputs to the tensor theory are the polymer matrix dielectric constant and conductivity, the analogous properties for the liquid crystal, and the characteristics of the liquid crystal droplets. Results are presented for the field and droplet concentration dependence of the dielectric constant and the droplet internal field for systems of: (a) radial droplets; (b) bipolar droplets with fixed axes parallel to the imposed field; and (c) bipolar droplets with sets of preferred local axes. Case (c) shows clearly that reorientation of droplet axes plays an important role in PDLC film response and optical properties.

[1] See e.g. P.S. Drzaic and A. Muller, Liquid Crystals, 5, 1467 (1989).

\* Permanent address: Institute of Surface Chemistry, Ukraine Academy of Science, Kiev, Ukraine

<sup>†</sup> Work supported by (UK) EPSRC Grant GR/J88111.

#### B1P.30

TRANSMITTANCE AND SPATIAL OPTICAL NOISE OF POLYMER DISPERSED LIQUID CRYSTAL LAYERS, <u>Valery A. Loiko</u>, Aleksander V. Konkolovich, Institute of Physics Academy of Sciences of Belarus, Minsk 220072, Scaryna Av., 68. Belarus.

On the base of the optical scattering medium methods transmittance and spatial noise spectrum thin polymer dispersed liquid crystal (PDLC) layer are determined. We take into account: optical properties of liquid crystal droplets in the controlling field; space fluctuations of the number of droplets along the surface, polidispersity of droplets, close topological ordering at high concentration of droplets. Model of stochastic amplitude phase screen [1] has been worked out. The result are analysed under the anomalous diffraction approximation and single scattering approximation for the PDLC layer of nematic spherical droplets. We considered different configuration of droplet's directors: radial, bipolar and homogeneous. Proposed model gives an opportunity for investigation of contrast and noise characteristics of thin PDLC layers, when the solution of the scattering problem for the separate (nematic, cholesteric, smectic) droplet is found. The results of this work allow one to make a forecast of above mentioned characteristics for thin layers for different practical situations.

[1] V. Loiko, A. Konkolovich, Opt. & Spectr. 77, 998 (1994).

#### **B1P.31**

THEORETICAL AND EXPERIMENTAL RESEARCH OF ANGULAR TRANSMISSION OF POWERED PDLC, <u>Giuseppe Chidichimo</u>, Ziqiang Huang\*, Fiore Pasquale Nicoletta and Giovanni De Filpo, Physical Chemistry Laboratory, Department of Chemistry, University of Calabria, 87030 Rende(CS), Italy.

Tilted transmission of full powered PDLC is calculated theoretically. Dimension of the droplets and difference of refractive indices between polymer and liquid crystal are found to be the most important facts that affect transmission. Experiments agree quit well with the theory. By regulating the parameters (such as dimension of the droplets, refractive indices, thickness of the sample and so on) of PDLC, one can find a theoretical curve that is best fitted to the experimental transmission. Comparison of best fitting parameters with measured values is presented.

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MORPHOLOGY OF POLYMER NETWORKS FORMED IN LIQUID CRYSTALLINE PHASES, C. V. Rajaram, and S. D. Hudson, Case Western Reserve U., Cleveland, OH 44106, and L. C. Chien, Kent State U., Kent, OH 44242, USA

The morphology of polymer networks formed by solution polymerization and phase separation is described. Various mesogensic diacrylate monomers were polymerized in isotropic, nematic and smectic phases of a liquid crystalline solvent. At early stages of the reaction, polymer particles phase separate. The aggregation of these particles to form a three dimensional network is reaction-limited apparently at short length and time scales, and diffusion-limited at longer times. This crossover in aggregation behavior gives a dimension characteristic of the network that can be determined by scanning electron microscopy. A model has been developed, consistent with observation, to describe kinetic factors that determine this crossover and control network morphology. A variety of morphologies have been obtained, depending on monomer structure and polymerization conditions. The influence of network morphology on electro-optic performance is presented.

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**B1P.33** 

HIGH-BIREFRINGENCE MESOMORPHIC "SIDE-ON" SYSTEMS FOR POLYMER-STABILIZED BROADBAND REFLECTIVE DISPLAYS, Nathalie Leroux, <u>Julie Cho</u>, L.-C. Chien\*, Liquid Crystal Institute, Chemical Physics and NSF ALCOM Center, Kent State University, Kent, OH 44242.

This paper describes the preparations of new mesogenic side-on materials and polymer-stabilized liquid crystals. Several laterally substituted bisnaphthalene tolane-based liquid crystal and acrylates (BNA) have been found to possess either nematic or chiral nematic phase, depending on the molecular structure. Side-on polymers, resulted from the polymerizations of BNAs, exhibited similar mesophases and high birefringence values as their mesogenic monomers. The incorporation of a BNA into a polymer-stabilized cholesteric display resulted in the broadening of reflection bandwidth.

This research was supported in part by the NSF ALCOM Center Grant DMR89-20147 and ARPA Low Power Displays Contract # N61331-94-K-0042.

**B1P.34** 

POLYMER STABILIZED STN DEVICES WITH WIDER VIEWING ANGLE
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\* Jilin University, Changchun 130022, P. R. CHINA

The polymer stabilized STN devices were prepared and its electro-optical response was studied. The experimental results show the polymer stabilized STN device has a lower threshold voltage and wider and nearly uniform viewing angular characteristics comparing with traditional STN devices. The measuring results of threshold voltage response time, viewing angle, contrast ratio and polymer network micro-structure and the interaction between polymer network and liquid crystals will be presented.

[1] P. J. Bos, et al., SID'93, P 877 (1993)

[2] D. S. Fredley, et al., IDRC'94, P 480 (1994)

#### POLYMER NETWORK STABLIZED DOUBLE-DOMAIN STN-LCD

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In a previous paper, the auther's research group have been proposed double-domain(DD) STN-LCD using double-rubbing technology that feature uniform and wide viewing angle characteristics[1]. There appeared domain-disclinations because of the difference of directors between neighbouring domains in DD-STN-LCD. Those disclinations caused E-O characteristic of DDSTN get worse. In order to slove this problem we propose a polymer network stablized(PNS) DD-STN-LCD. By curing a photo LC diacrylate disolved into a STN liquid-crystal under the controlled applied electric field, we can improve the pretiltangle of LC molecules up to 20°, then those domain-disclinations were eliminated partly and the E-O characteristic of the device was improved.

[1] Ma Zhenjun, Ma Kai et al, has been accepted by SID'96."

**B1P.36** 

#### POLYMER NETWORK STABILZED SBE-LCD

Q.B. Wang, R.P.Sun, Y.Q.Tian, X,M.Huang LC Lab of Changchun Institute of Physics, P.R.China, Changchun 130021

Our research group had reported that the pretilt angle of LC molecules can be improved with polymer network use common polyimide alignment layers[1]. Supertwisted birefringent effect (SBE) LCD with a 270° twist require pretilt angles of about 20° in order to eliminate stripe formation[2]. We doped a UV-curable diacrylate monomer in SBE cell with common alignment layers and cured under a controlled applied electric field. A polymer network stablized (PNS) SBE device with good steepness of the electrocapacitance response was obtained. The stripes were eliminated because of a very high pretilt angle stabilized by polymer network.

[1] Q. Wang, R.Sun, Y.tian, X.Huang, has been accepted by SID'96. [2]T.J.Scheffer and J.Nehring, Appl.Phys.Lett. 45(1984)1021.

#### **B1P.37**

EFFECTS and STRUCTURAL RELATIONSHIP OF SURFACTANT ON PDLC HYSTERESIS CONTROL, <u>David B. Chung\*</u>, Hideaki Tsuda, Hideo Chida, and Akihiro Mochizuki, Fujitsu Limited, 10-1 Morinosato-Wakamiya, Atsugi 243-01, Japan

There are numerous reports in the literature dealing with the electro-optical properties of PDLC with experiments designed to reduce the material's hysteresis<sup>(1-3)</sup>. They suggest strong interaction relationship between the liquid crystals and the polymeric materials. We present the approach of lowering hysteresis of the PDLC films based on experimental work in the surfactant relationship with the polymer dispersed material matrix. Experimental results and structural relationship will be described.

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<sup>&</sup>lt;sup>1</sup> H. Hirai et al, Proc. of 17th Liquid Crystal Symposium, Sapporo, Japan 4F115 (1991)

<sup>&</sup>lt;sup>2</sup> N. Yamada, T. Hirai, N. Ohnishi, S. Kouzaki, F. Funada, & K. Awane, In Japan Display 1992, pp. 695-698

<sup>&</sup>lt;sup>3</sup> L. Bouteiller, P. Lebarn, F. Massie & P. Robin, Europe Display 1993, pp.325-328

HIGH MEMORY EFFECTS IN POLYMER DISPERSED CHOLESTERIC LIQUID CRYSTALS, P.Sixou, J.Nourry and A.Magnaldo, L.P.M.C., CNRS URA190, F-06108 Nice Cedex 2, FRANCE.

A cholesteric liquid crystal with negative dielectric anisotropy and with a visible wavelength selective reflection was encapsulated in a polymer film. When an appropriate field is applied, the film becomes reflective at the same wavelength as the non-encapsulated cholesteric mixture. This reflective state relaxes to a memory state after having removed the field, by losing only 5% of its' direct normal reflection level, and losing practically no direct-direct transmission. Moreover, this state is stable over months. The initial state, i.e. the state before the field was applied, is retrieved after heating the sample above its' cholesteric to isotropic transition temperature and cooling. The same cycle can be repeated. The memory effect is more or less high, depending on the physical parameters during elaboration of the films.

The memory state, and the states corresponding to decreasing memory effects, were characterized by spectral direct-hemispherical and direct-direct transmissions, direct-normal reflection, response time and voltage response measurements. A simple model was derived, which tries to explain how the cholesteric droplet relaxes after removal of the electric field, with or without memory effect.

B1P.39

LASER ADDRESSED INFORMATION RECORDING IN BISTABLE PDChLC FILMS, S.L.Smorgon, V.A.Zhuikov, V.Ya.Zyryanov and <u>V.F.Shabanov</u>, L.V.Kirensky Institute of Physics, Krasnoyarsk, 660036, Russia.

Polymer dispersed cholesteric liquid crystal (PDChLC) films exhibiting a large hysteresis of the volt-contrast curve were used for laser addressed information recording. Switching over of the bistable state was provided by a local heating of the PDChLC film due to the thermal effect of the light. A proper dye was added to ChLC to increase the light absorption and thus improve sensitivity of the method. Unlike the photoaddressed method [1], here recording is possible not only in a normal mode (a transparent spot against a scattering background), but in a reverse mode too. With this method no photoconductive layer is required in the cell design. Image recording with grey levels was obtained by varying the duration or the amplitude of the laser pulse.

[1] H.Fujikake, K.Takizawa, H.Kikuchi, T.Fujii, SID 93 Digest, 24, 873 (1993).

B1P.40

LC MATERIAL STUDIES FOR 3D-IMAGE DEVICES WITH THE PSCT, G.M.Zharkova, I.V.Samsonova, S.A.Streltsov, and I.Sh.Shteinberg\*, Institute of Theoretical and Applied Mechanics SB RAS, Institutskaya Str., 4/1, 630090, Novosibirsk, Russia, \* Institute of Automation and Electrometry SB RAS, Universitetskii Av., 1, 630090, Novosibirsk, Russia.

We have studied the properties of material with the polymer stabilized cholesteric texture (PSCT) [1] for creation of 3D images. Morphology, volt-contrast and dynamic features of composite films containing polyvinylpyrrolidone and nematic liquid crystal with active dopes have been studied for a wide range (2-5% polymer, 10-15% active dopes) of film composition. The effects of frequency and voltage of applied a.c. electric field on the transmittance and response times were measured for films with 2% polymer and 10% active dopes where the maximum optical contrast was observed. The properties of a number of sequentially positioned LC displays containing these composites for creation of 3D static and dynamic images were studied by means of fast-response acousto-optical deflectors.

[1] D.-K.Yang, L.-C. Chien, and J.W.Doane, Conf. Res. IDRC. SID, San Diego, CA, 1991, p. 49.



THE RELATIONSHIP BETWEEN CONTACT ANGLES AND CHARACTERISTICS OF Ch-LIQUID CRYSTAL/POLYMER COMPOSITE FILMS, K.Hashimoto, T.Hatano, N.Kobayashi, M.Okada and N.Masazumi, Minolta Co., Ltd., 1-2 Sakura-machi, Takatsuki-Shi Osaka 569, Japan.

Bistable Ch-liquid crystal/polymer composite films were prepared. Their reflection wave length was controlled in infrared region and switching between transparency and scattering states; that is, Black/White mode displays can be attained. Contrast ratios and transparency of the composite films depend on liquid crystal materials, polymer materials and morphology of the films. In addition, relations between contact angles of Ch-liquid crystal/polymer interface and characteristics of the composite films are investigated. It is found that as the contact angles of Ch-liquid crystal/polymer interface decrease the contrast ratios and transparency of films increase. In as the contact angles decrease, where small contact angle makes a Ch-liquid crystal to form a planar texture easily and because of that the contrast ratios and transparency of films increase.

#### B1P.42

EFFECT OF THE ADDITION OF A SMALL AMOUNT OF MESOMORPHIC POLYMER ON THE ELECTRO-OPTIC BEHAVIORS OF A POLYMER NETWORK LIQUID CRYSTAL, J. Nourry, A. Magnaldo, and P. Sixou, Laboratoire de Physique de Matière Condensée, CNRS URA 190, Université de Nice-Sophia Antipolis, F-06108 Nice Cedex 2, FRANCE.

We investigated optical morphologies and electro-optical performances when we substituted a small part, from 1 to 3%wt, of the resin matrix by a liquid crystal polymer. Liquid crystal polymers were either nematic or cholesteric. Results showed that when we irradiated the mixture under an high enough electric field, we managed to freeze current induced instabilities embedded in the liquid crystal inclusions. Measurements were carried out concerning electro-optics performances of mixtures when varying the amount of the liquid crystal polymer. We studied their transmittivity and their dynamic responses (rise and decay times). Observations guessed that the mesomorphic polymer played the same role as a surfactant. It increased the average size of the liquid crystal inclusions enhancing for example the transmittivity of the system. As far as the decay time was concerned, figures seemed to show two relaxation times. Analyzing their values might lead us to understand the very role played by the polymer additive. It could be a way to clarify the nature of the anchoring forces inside liquid crystal inclusions.

#### B1P.43

POLYMER MORPHOLOGY AND ELECTRO-OPTIC PROPERTIES OF PSCT DEVICES T. Nakata\*, T. Gotoh, M. Satoh, E. Hasegawa, Functional Devices Res. Labs., NEC Corporation, Kawasaki, Kanagawa, 216, Japan.

The electro-optic properties and polymer morphology of a polymer stabilized cholesteric textures (PSCT) device[1] have been investigated. Polymer morphology was shown by scanning electron microscopy to be three-dimensionally networked spherical particles with diameter of submicron order. The particle diameter, the shape and the distance between neighboring networks varied with polymerization conditions, the molecular structure and concentration of the prepolymer. These factors affected the electro-optic properties, i.e., driving voltage, hysteresis width and contrast ratio. The best electro-optic properties were obtained in a PSCT device with polymer morphology of mean particle diameter of 0.15 µm and mean network distance of 1.2 µm. This morphology was formed by curing 4,4'-Bis(acryloyloxy)diethylstilbene prepolymer under low-UV-intensity irradiation. The results in this study offer increased flexibility in designing PSCT devices.

[1] J. W. Doane, D.-K. Yang and L.-C. Chien. Conference Record of the IDRC, SID, 175 (1991).

ANNEALING AND MEMORY EFFECTS IN POLYMER DISPERSED CHOLESTERIC LIQUID CRYSTALS, A. Magnaldo, J.Nourry and P. Sixou, L.P.M.C., CNRS URA 190, UNSA, F-06108 Nice Cedex 2, FRANCE.

A cholesteric liquid crystal with negative dielectric anisotropy and with a visible wavelength selective reflection presents high memory effects when encapsulated in a polymer film. Three states are accessible: reflecting state, memory state and refreshed state. The two last states are stable over months. When the sample is annealed for a few seconds, the sample goes through an irreversible transformation, after which the memory state is no longer accessible. Through the data collected as samples were progressively annealed, such as threshold voltages, response times, reflection wavelengths and memory coefficients, it was guessed how annealing changes the film properties.

The physical phenomena occurring is a two step process. For short annealing times (seconds) sharp changes in response times and memory coefficients indicate changes at the droplet-matrix interface region. The longer annealing times (minutes) correspond to changes more deeply inside the matrix, which influences above all the threshold voltages and spectral characteristics.

At last, we used dual frequency liquid crystals as a prospecting tool to try to understand what happens at the droplet-matrix interface as the memory effect is lost.

B1P.45

# A CASE OF MISTAKEN IDENTITY: SPONTANEOUS FORMATION OF TWISTED BIPOLAR DROPLETS IN ACHIRAL NEMATIC MATERIALS. Paul Drzaic, Raychem Corporation, Menlo Park CA 94025 USA

In 1988 it was reported<sup>1</sup> that droplets of liquid crystal with a bend to splay ratio  $(K_{33}/K_{11})$  less than 1.0 spontaneously formed a concentric director field, with the liquid crystal arranged in concentric circles around a central core line defect. New interpretation of these systems reveals that the director field within these droplets actually forms a twisted bipolar structure. The formation of twisted structures out of achiral material has been observed in some nematic systems before, <sup>2</sup> and the stability criteria for these structures have been predicted by Williams.<sup>3</sup> Here I show that the formation of twisted structures in low  $K_{33}/K_{11}$  material is consistent with the Williams stability criteria. The structures here will be compared to other observations of the twisted bipolar structures.<sup>4</sup>

1) P. S. Drzaic, Mol. Cryst. Liq. Cryst., 1988. 154, 289-306. 2) G. E. Volovik and O. D. Lavrentovich, Sov. Phys. JETP, 1983. 58, 1159-1166. 3) R. D. Williams, J. Phys. A: Math. Gen., 1986. 19, 3211-3222. 4) O. D. Lavrentovich and V. V. Sergan, Il Nuovo Cimento, 1990. 12, 1219-22.

**B1P.46** 

DIELECTRIC STUDY OF TRANSITIONS BETWEEN CHOLESTERIC TEXTURES AND DESIGN OF DYNAMIC DRIVE SCHEME, <u>Xiao-Yang Huang</u>\*, Deng-Ke Yang, Phil Bos, and J. William Doane, Liquid Crystal Institute and Department of Physics, Kent State University, Kent, OH 44240, USA.

Field-induced transitions between homeotropic, focal conic and planar textures of cholesteric liquid crystals are studied with transient dielectric measurement. At a low bias voltage, the homeotropic-planar transition proceeds in two steps: homeotropic to transient planar and transient planar to stable planar texture. The homeotropic-transient planar transition is in the order of 1 ms. At a high bias voltage, homeotropic-focal conic transition proceeds in a time interval of 100 ms. Hysteresis is observed between the homeotropic and focal conic textures. Based on these experimental results, the dynamic drive scheme is designed for bistable reflective cholesteric displays. The addressing speed is improved by a factor of 50.

<sup>\*</sup> Present address: Kent Display Systems, Inc., 343 Portage Blvd., Kent, OH 44240, USA.

THE MECHANISM FOR THE FORMATION OF POLYMER WALL IN HIGHER POLYMER CONTENT CHOLESTERIC LIQUID CRYSTAL MIXTURE, Y. Ji, J. J. Francl and J. L. West, Liquid Crystal Institute, Kent State University, Kent OH, 44242, USA.

We have investigated the formation of polymer walls in higher polymer content cholesteric liquid crystal formulations [1]. The mechanism of polymer wall formation including phase separation and polymer diffusion are complex. We found that it is possible to regulate the polymer wall morphology by controlling the photopolymerization process. The polymer wall density increased with increasing concentration of monomer(s) in the mixture. Also, the temperature, UV light intensity, exposure time, and the ratio of the exposure area and the masked area all affect the wall formation process.

[1] Y. Ji, J. J. Francl, W. J. Fritz, P. J. Bos, J. L. West, SID Digest of Technical Papers, 1996 \* Supported by ARPA Grant N61331-94-K-0042

#### **B1P.48**

DYNAMIC HOLOGRAPHIC GRATINGS IN NEMATIC CELL WITH PERIODIC BOUNDARY CONDITIONS, D.Andrienko, M.Lednei, and I.Pinkevich, Department of Physics, Kiev University, Glushkova prospect 6, Kiev 252127, Ukraine.

The homeotropic nematic cell is considered in which the light intensity spatial grating is created. In this case the director interaction with a light field leads to the director periodic distribution in the cell volume [1]. It is investigated the influence of the spatial periodic change of the director anchoring energy value or the director easy orientation axis at the cell surfaces on the director spatial distribution in the cell volume under the action of the above mentioned light field. It is shown that in both cases for the non threshold interaction the director distribution takes the form of a superposition of the cosine gratings with different periods which are the linear combinations with the whole number coefficients of the light intensity and boundary conditions periods. The diffraction efficiency of the gratings is evaluated. The gratings with the biggest periods have the greatest diffraction efficiencies. The lightinduced Freedericksz transition threshold value in the nematic cell with periodic boundary conditions is obtained as well.

[1] V.Yu.Reshetnyak, I.P.Pinkevich, and M.F.Lednei, Mol.Cryst.Liq.Cryst.261, 147(1995).

#### B1P.49

SPONTANEOUS TWIST IN THE NEMATIC PHASE OF TRANS-4-ALKYL CYCLOHEXANECARBOXYLIC ACIDS' DIMERS, S. I. Torgova[1], A. Sparavigna[2], L. Komitov[3], and A. Strigazzi[2]. <sup>1</sup>Organic Intermediates and Dyes Inst., Moscow, Russia, <sup>2</sup>Dip. di Fisica, Politecnico di Torino, Torino, Italia, <sup>3</sup> Physics Dept., Chalmers University of Technology, Goeteborg, Sweden. Sandwich cells with gap less than 2  $\mu$ m were filled with cyclohexanecarboxylic acids and investigated by polarizing microscopy. The inner surfaces of the cells were covered by a thin polyimide layer buffed unidirectionally in order to achieve a uniform planar alignment of the substance in the nematic phase. On cooling from the isotropic phase, two type of nematic domains with different alignment were found to grow, unidirectional planar in different cell places with different twist sense, twisted domains always emerged thus they can not be regarded as induced by the surface aligning film. With the coalescence of the nematic droplets floating in the isotropic sea, the number of the very quickly decreased, the twist alignment transforming into a twisted domains uniform planar one. A model describing the phenomenon is given.

BIDIMENSIONAL STRIPES IN HYBRID ALIGNED NEMATIC CELL FILLED BY 5CB, A. Sparavigna<sup>1</sup>, O.D. Lavrentovich<sup>2</sup>, A. Strigazzi<sup>1</sup>, <sup>1</sup> Dipartimento di Fisica, Politecnico di Torino, Torino, Italia, <sup>2</sup> Liquid Crystal Institute, Kent State University, Kent OH, USA

It is well known that the precursor of a 5CB nematic droplet put onto a glycerin flat surface behaves as a wedge-shaped hybrid layer, strongly anchored for tilt but with azimuthal degeneration at the planar wall. In such a geometry, the arising of unidimensional stripes was demonstrated [1-2]. We show here that in certain conditions a bidimensional stripes texture appears, and that the surface-like elastic constant  $K_{24}$  plays an important role in such a phenomenon.

[1] O.D. Lavrentovich and V.Pergamenshchik, Mol. Cryst. Liq. Cryst. 179, 125 (1990); [2] A. Sparavigna, O.D. Lavrentovich and A. Strigazzi Phys. Rev. E 49, 1344 (1994); Phys. Rev. E 51, 792 (1995)

B1P.51

CONDUCTING POLYMERS AS ALIGNMENT LAYERS AND PATTERNED ELECTRODES FOR TWISTED NEMATIC LIQUID CRYSTAL DISPLAYS, Jerome B. Lando, Andy Chang, Chin-Jen S. Tseng, Department of Macromolecular Science, J. Adin Mann, Jr., Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, David Johnson, Department of Physics, Kent State University, Kent, OH 44242, USA.

Initial work was performed on the preparation of poly(p-phenylene vinylene) and poly(p-phenylene) alignment layers for twisted nematic liquid crystal displays. Soluble precursor amphiphilic polymers, spread at the gas-water interface, were aligned during Langmuir-Blodgett deposition. The structure of the precursor multilayers has been investigated before and after curing of the multilayers to the desired polymers. Initial tests have indicated that the precursor multilayers are good alignment layers for liquid crystal displays.

B1P.52

NEGATIVE Δ n COMPENSATORS FOR IMPROVEMENT OF LCD ANGULAR DEPENDENCY

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Corporation, 4-1-1 Miyazaki, Miyamaeku, Kawasaki, Kanagawa 216 JAPAN

In order to improve LCD angular dependency, an ideal compensator can be designed, which has an optical axis profile similar to a liquid crystal director profile in the LCD and is composed of negative  $\Delta$  n elements. This design procedure can be applied to a normally black twisted nematic (NB-TN) case. We numerically simulated angular dependency for compensated and uncompensated NB-TN cases. The simulation results show this compensator increases contrast ratio in all azimuth directions except for the direction which corresponds to the mid-plane LC director orientation.

CHARACTERISTICS OF LIQUID CRYSTAL DISPLAY FABRICATED BY ALIGNMENT TRANSCRIPTION METHOD, Y. Toko, B. Y. Zhang, T. Sugiyama, K. Katoh, and T. Akahane\*, R&D Laboratory, Stanley Electric Co., Ltd., Yokohama, 225, Japan, \*Department of Electrical Engineering, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan.

We have developed a novel fabrication method of an LCD without rubbing treatment on the substrate surfaces of the cell. In this method, LC alignment is transcribed from an original rubbed substrate to the counter substrate that is coated with non-rubbed polymer, and is fixed on the surface by memory effect of the interface between LC molecules and the polymer surface. This transcribed and memorized alignment on the non-rubbed polymer is rather stable. Therefore, it is possible to fabricate the LCD by putting the copied polymer substrate separated from the original substrate upon another substrate. It is found that the LCDs having any alignment such as multi-domain structure [1] can be made easily without generating dust and static electricity caused by the rubbing. This fabrication process and characteristics of the LCD made by this method will be described.

[1] T. Sugiyama, Y. Toko, T. Hashimoto, K.Katoh, Y. Iimura, and S. Kobayashi, SID'94 Digest, 25, 919 (1994).

#### **B1P.54**

THE EFFECT OF MATERIAL PARAMETERS ON THE HYSTERESIS OF STN DISPLAYS J. Li, C. D. Hoke and P. J. Bos, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA.

We have investigated the hysteretic electro-optic behavior of STN displays with the twist angles larger than 270°. This effect was discovered in early 1980s. <sup>12</sup> Recently, the interests on the subject increases due to their low driving voltage and fast switching speed. <sup>3,4,5</sup> They are also disclination-free. In this study, a pair of Lagrange's equations based on the continuum theory were solved numerically. The Gibbs energy and elastic energy of the nematic liquid crystal medium under the influence of external electric field were calculated. The director configurations at an applied field may be significantly different depending on the initial conditions. The elastic energy of the liquid crystal medium is used to describe its bistability. The effects of cell twist angle, elastic constants, thickness to pitch ratio, dielectric parameter, and surface pretilt angle are presented.

Research supported by NSF ALCOM Center under the grant #89-20147

- D. W. Berreman and W. R. Heffner, Appl. Phys. Lett., 37, 109(1980)
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J. Li, C. Hoke, D. S. Fredley, and P. J. Bos, SID '96, S18.3, (1996)

#### **B1P.55**

LIQUID CRYSTAL MODULATOR FOR FIBER COMMUTATION CHANNELS, Yu.V. Razvin, A.A.Kovalev and V.A. Potachitz, Institute of Electronics, Belarus Academy of Sciences, 22 Lagoiski Trakt, Minsk, 220841, Republic of Belarus

The results of the development and investigation of the modulation characteristics of a coaxial liquid crystal modulator are presented. The active part of the modulator under investigation is implemented on the basis of a "cylindrical geometry". Specific design solutions of such a coaxial modulator are considered. It is shown that in the case under study the modulation depth increases 2 or 3-fold as compared with conventional LC modulators [1] and exceeds 50%, noise level becoming lower. Prospects of using such modulator for interelement fiber commutation channels in optical memory systems are discussed.

1. Ch. Veilleaux et al. Optics Letters, 11, 733-735 (1986).

A NEW REFLECTIVE GUEST-HOST DISPLAY INCORPORATING A LIGHT CONTROL FILM, <u>Hidehiro SEKI\*</u>, Norio SUGIURA, Masahiro SHIMIZU, and Tatsuo UCHIDA, \*Hachinohe Inst. of Tech., Tohoku University, JAPAN

A bright reflection type LCD without a backlight is a key device of a for portable information systems. This paper proposes a new Guest-Host type liquid-crystal display. It consists of a light control film (LCF: supplied by Sumitomo Chemical Industry Co., Ltd.), a phase change type Guest-Host (PCGH) liquid-crystal layer and a mirror substrate. LCF scatters only incident light from particular angles and transmits incident light from other angles. The experimental results show that the brightness of the new device is approximately ten times higher than a MgO-standard white. The device does not need a polarizer that absorbs at least half of the incident lights. The structure is simple in comparison to the reflection type PCGH-LCD with a geometrically controlled reflection mirror [1]. Optimization of the characteristic of LCF in the new device will promise a very bright reflection type LCD.

[1] N. Sugiura and T. Uchida: Digest of AM-LCD, P4-1, p.153 (1995).

B1P.57

• NEMATIC OPTICAL DIODE, R. Klouda<sup>1</sup>, V.G. Nazarenko<sup>1</sup>, and O.D. Lavrentovich<sup>1,2</sup>, <sup>1</sup> Liquid Crystal Institute and <sup>2</sup> Chemical Physics Program, Kent State University, Kent, OH 44242, USA\*.

We report on a unipolar electrooptic effect in a homeotropic nematic layer with a positive anisotropy of dielectric permitivity and conductivity. The effect appears in an external static electric field. The cell behaves as an "optical diode": it is transparent for polarized light if the "positive" voltage is applied but blocks the light when the opposite "negative" voltage is applied. The physical mechanism of the unipolar effect is the net surface electric polarization achieved by treatment of the two opposite plates with different homeotropic coatings.

The work was supported by NSF ALCOM Center Grant DMR-20147.

B1P.58

THE RETARDATION EFFECT OF DIELECTRIC RELAXATION ON THE ULTRA FAST SWITCHING OF NEMATIC LIQUID CRYSTALS, Z. Zou, G.M. Danner, H. Takanashi\*, J.E. Maclennan, and N.A. Clark, University of Colorado, Physics Department and OCS Center, Boulder, CO 80309, USA.

Very fast switching (≥ 10nsec) has been obtained in our group by applying high electric field pulses to a nematic cell. In the fast switching region, the time dependence of dielectric constants must be included when calculating the reorientation dynamics. In this work we theoretically calculate the temporal response for pretilted planar nematic 5CB cell including dielectric relaxation effects. By employing the actual voltage applied to the cell, the calculated optical response will be compared with the measurement as a function of applied field and temperature.

This work is partially supported by CATI 960002 and NSF MRG Grant DMR 9224168.

\*Central Research Lab, Sony Corp., Tokyo, Japan.



MULTIDOMAIN STRUCTURES FOR IMPROVED VIEWING ANGLE TN LCDS Rob van Asselt, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

The orientation of nematic liquid crystals on spherulitic polymers was studied, in order to obtain LCDs having wide and symmetric viewing angles. Both a radial and a concentric director pattern could be obtained on spherulitic polymer films, depending on the type of polymer used. These orientations result in symmetric viewing angle characteristics and no greyscale inversion up to polar angles of 50 degrees.

Advantage of this method is rubbingless orientation of liquid crystals, with a gradual change of the director pattern. Therefore the number of bright disclination lines formed in the addressed state is reduced, as compared to amorphous TN.

#### **B1P.60**

PHYSICAL BEHAVIOR OF NEMATIC LIQUID CRYSTALS USING IN-PLANE SWITCHING MODE, Masahito Oh-e\*, Masuyuki Ohta\* and Katsumi Kondo\*\*, \*Electron Tube & Devices Division, Hitachi, Ltd., 3300 Hayano Mobara-shi, Chiba-ken, 297 Japan, \*\*Hitachi Research Laboratory, Hitachi, Ltd., 7-1-1 Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan

We have investigated the switching and response mechanism of the in-plane switching (IPS) mode which is a novel technique for wide viewing-angle liquid crystal displays [1-3]. In the IPS mode, an electric field is supplied to the liquid crystals along the direction parallel to the plane of the substrates. First, it was made clear that it was the electric field and not the voltage that drives the liquid crystals in the IPS mode [2]. Significantly, an inversely proportional relationship between the threshold voltage and the cell gap was found to hold. Second, the relaxation time of the liquid crystals when removing the electric field was described as a proportional relationship to the second power of the liquid crystal layer thickness. A thinner cell gap is also proved to be effective to obtain fast response time in the IPS mode. By contrast, the field strength governs the switching-on time when applying the in-plane electric field.

[1] R. Kiefer, B. Weber, F. Windsceid and G. Baur, Proc. of the 12th IDRC p. 547 (1992). [2] M. Oh-e, M. Ohta, S. Aratani and K. Kondo, Proc. of the 15th IDRC, p. 577 (1995).; M. Oh-e and K. Kondo, Appl. Phys. Lett., 67, 3985 (1995). [3] M. Ohta, M. Oh-e and K. Kondo, Proc. of the 15th IDRC, p. 707 (1995).

#### **B1P.61**

FAST SWITCHING OF STLM VALVES OPERATING ON THE BASIS OF TWIST EFFECT IN LIQUID CRYSTALS, A.A. Kovalev, Yu.V. Razvin and V.A. Potachitz, Institute of Electronics, Belarus Academy of Sciences, 22 Lagoiski Trakt, Minsk, 220841, Republic of Belarus.

This paper presents the results of investigation of the modulation characteristics of the STLM light valves based on twist-effect under conditions of initial distortion of LC-layer director that is caused by contact of the liquid crystal with the periodic structure of the modulator electrodes. When the directions of planar orientation of LC molecules and electrodes on the STLM substrate do not coincide, in the near-electrode regions there occur initial director distortions which propagate to the depth of the LC layer due to elastic forces. Modulation of the light flux is effected due to deformation of the disturbed near-electrode layer in the field of control pulse. The deformed layers strongly bound with the orienting coating result in a fast relaxation of LC molecules into initial state after electric field is switched off [1]. Such mechanism of light modulation makes it possible to decrease the ON/OFF cycle of the STLM's row down to 10 % with a contrast being about 100:1. This paper includes a comparison of contrast-time characteristics of the STLM valve switching for various methods of setting initial distortions of the LC director.

[1] A. Kovalev, Yu. Razvin, V. Potachits, Proc. of the Academy of sciences of Belarus N1,58(1994).

DYNAMIC OPTICAL RESPONSE OF A TWISTED NEMATIC DEVICE, Jack R. Kelly and Syed H. Jamal, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

We have performed detailed numerical modeling and characterization of the dynamic optical response of a 90° twisted nematic, including flow. We have found that it is possible to obtain excellent agreement between model and experiment - at all voltages and all viewing angles - with only two viscosity parameters; these are the Leslie coefficient  $\alpha_2$  and the sum of two others,  $\alpha_4+\alpha_5$ . Hence a detailed knowledge of all 5 Leslie coefficients is not needed. The origin of these results is illucidated in terms of an effective viscosity. An outgrowth of this analysis is a prescription for improving turn-off speeds through proper tailoring of the viscosities.

**B1P.63** 

### A NEW 2 x 2 MATRIX REPRESENTATION FOR TWISTED NEMATIC LIQUID CRYSTAL DIAPLAYS AT OBLIQUE INCIDENCE

A. Lien, IBM Research Division, Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, NY 10598

C.-J. Chen<sup>a</sup>), Department of Chemical Engineering and Material Science, University of Minnesota, Minnesota, Minnesota 55455

A new 2 x 2 matrix representation for the twisted nematic liquid crystal display (TN-LCD) at oblique incidence was obtained. Compared with the previous representation developed by Lien [Appl. Phys. Lett. 57, 2767 (1990) and SID 91 Digest, 586 (1991)], the optical transmissions calculated by this new 2 x 2 matrix method are much closer to those calculated by the 4 x 4 matrix method with spectrum averaging to account for the nonzero bandwidth of the incident light. The discrepancy between the last two is generally less than 1 %. The simplicity and accuracy makes this new 2 x 2 matrix method very useful. Both formulation and application to real cases will be discussed.

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B1P.64

FILM COMPENSATED EFFECTS ON BEND ALIGNMENT LIQUID CRYSTAL DISPLAYS, C.-J. Chen\*, Department of Chemical Engineering and Materials Science, University of Minnesota, Minnesota, Minnesota 55455 and A. Lien, IBM Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, NY 10598

The compensation effects of a single biaxial film and the combination of two uniaxial films on a bend alignment liquid crystal display (LCD) were studied based on our recently developed propagation matrices for biaxial media.[1] It was found, at the principal planes, the compensation effects of a biaxial film are the same as those of two properly chosen uniaxial films, in which one has rod-like, while the other has disc-like index of ellipsoid. However, their compensation effects at other planes are generally different. This mismatch is a general property because the birefringence for each viewing plane has its own angle dependence. Once the optical axes of the two uniaxial films are decided, so do the relations among the birefringent angle dependences for all viewing planes. The relations of birefringent angle dependences for one optical system are generally different from those of the other. It is impossible to match all birefringent angle dependences for these two optical systems due to the limited adjustable parameters.

<sup>[1]</sup> C.-J. Chen, A. Lien, and M. I. Nathan, SID Digest in press (1996).

<sup>\*</sup> Supported by IBM Thomas J. Research Center



BISTABLE NEMATIC AND CHOLESTERIC DISPLAYS STABILZED BY REBUILDABLE NETWORKS OF PYROGENIC SILICA M. Kreuzer, M. Bittner, T. Vogeler, and F. Simoni\*, Technische Hochschule Darmstadt, Institute of Applied Physics, Hochschulstraße 6, 64289 Darmstadt, Germany, \* Universitá di Ancona, Dipartimento dei Materiali e della Terra, Via Brecce Bianche, 60131 Ancona, Italy.

During the last years intensive work has been done to use the properties of polymer networks to stabilize textures or to modify the electro-optical properties of liquid crystals (LC). A new approach is introduced with Filled Nematics consisting of a dispersion of a low volume fraction of pyrogenic silica (Aerosil) in the nematic phase of a LC. Aggregates of the nanometer-sized silica particles form a rebuildable network of agglomerates dividing the LC into nematic domains. The unique properties of the rebuildable network allow to stabilize any orientation of the nematic domains. This is exploited in building high resolution laser addressed displays. We studied experimentally and theoretically the laser writing process and used the results to increase the contrast ratio as well as the sensitivity by using small amounts of chiral dopants. First results on stabilizing cholesteric textures for bistable direct view displays will be presented The strong influence of the material and preparation parameters is investigated on a microscopic scale by surface induced second harmonic generation.

#### **B1P.66**

SYSTEMS "FILM SEMICONDUCTOR - LIQUID CRYSTAL - CONDUCTOR". Z.Gotra, O.Petriv, D.Batbayar. State University "Lvivska Politechnika", Bandera Str., 12, Lviv, Ukraine, 290646.

Analog liquid crystal display (ALCD) based on "film semiconductor - liquid crystal - conductor" structure type was investigated. Dependences of electrooptical characteristics to upon parameters dysplay were of semiconductor and liquid crystal layers of this the properties of these that It shown Was investigated. structures are determined by the process of contact semiconductor with liquid crystal, where double electrical layer, which has high electrical durability is formed&

STUDIES ON THE PERFORMANCE OF s-BLMs MODIFIED WITH LIQUID CRYSTALLINE CROWN ETHERS. Yu-E HE. and Ming-Gui XIE\*. Department of Chemistry. Sichuan University. Chengdu 610064. P. R. China.

We had found that the crown ether lyotropic liquid crystals could been prepared from the crown ether thermotropic liquid crystals. The liquid crystalline crown ether-modified self-assembled solid supported bilayer lipid membrances (s-BLMs) have been reported as sensitive and selective electrochemical probes for K<sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup>, Li<sup>+</sup>. The stability and electrochemical characteristics of the s-BLMs depended on the variety of metalic wire. organic soluent, lipids and molecular structure of mesomorphic crown ethers. The selectivity of ions were mad up the the ether ring of liquid crystalline crown ethers.

(1) Yu-E HE. Ming-Gui XIE. Angelica Ottava and H. Ti Tien. Anal. Lett.. 1995. 28 (3). 443-450. \* Project supported by National Natural Science Fondation of China.

**B2P.02** 

INCORPORATION OF THERMOTROPIC LIQUID CRYSTALS IN PHOSPHOLIPID MONOLAYERS: NECESSARY CONDITIONS OF HOMEOTROPIC ANCHORING, U. Kühnau, S. Wurlitzer, and H. Schmiedel, Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik I, Linnéstr. 5, 04103 Leipzig, Germany.

We investigated the phase behaviour of pure lipid- and mixtures of lipid/thermotropic LC monolayers by means of Langmuir-technique [1] and Brewster angle microscopy. Moreover, we determined the surface elastic energy of LC cells, the surfaces of which were prepared by means of Langmuir-Blodgett-technique with pure and with LC mixed amphiphiles of various molecular areas.

In our contribution we will show that an essential prerequisite for the homeotropic anchoring is the incorporation of thermotropic LC's in the oriented surface monolayer. This incorporation induces a phase transition in the interface monolayer and in this way, the bulk director of LC will be oriented normal to the surface [2]. Furthermore, we will discuss the reasons why the surface LC anchoring energy is a function of area per molecule in the deposited monolayer and why only definite kinds of liquid crystals orient homeotropically.

Our results are supported by DSC-, NMR- and X-ray experiments on bilayer systems.

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**B2P.03** 

LYOTROPIC LIQUID CRYSTALS: STRUCTURAL MESOMECHANICS, <u>D.B. Berg</u>, Laboratory of Applied Biophysics, Urals State Technical University, Yekaterinburg, 620002, RUSSIA.

The behaviour of the interphase boundary "solid crystal (SC) – lyotropic liquid crystal (LLC)" mechanical movement was investigated at the process of the physical growth of nonmesogenous SC in LLC medium. LLC structure levels mesomechanics paradigm: microlevel – structure elements (separate molecules, micelles etc.); mesolevel – mesophases (structure elements packing); macrolevel – textures (space filling by mesophases), was used for results interpretation. Computer experiment made it possible to obtain the number of SC growth shape morphotypes and to illustrate, that under certain conditions this shape can have fractal morphology. For investigation of the aggregation process the NaCl SC growth in thin LLC film ("NaCl-egg lecithin-water" system) was taken [1]. Fractal and dendrite crystal shapes growth conditions are described. Effect of mesophase transition "vesicular solution – lamellar phase" LLC inducing by the moving interphase boundary "crystal – solution" without external physical field is discovered. Boundary influence is verificated by the quantitative analysis of polarized light transmittence through the LLC texture [2], by the texture optical unipolar parameter calculation [3].

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PRESSURE-INDUCED LAMELLAR ORDER IN THE ISOTROPIC PHASE OF THE BILE SALT/LECITHIN SYSTEM, <u>Joseph T. Mang</u> and Rex P. Hjelm, MLNSC, Los Alamos National Laboratory, Los Alamos, NM 87545-1663 USA.

Small angle neutron scattering (SANS) has been employed to investigate the pressure and temperature dependence of the bile salt (BS) lecithin system. This system, while being of great interest to the medical community in the development of drug therapies, addresses the basic issues of self-assembly in complex fluids. The sample studied was a mixture of the bile salt, glychocolate, and lecithin in  $D_2O$  ( $\Gamma=0.8,\ 2$  g/l), corresponding to, at ambient pressure, the mixed vesicle region of the isotropic (I) phase. Upon increasing the hydrostatic pressure, interesting morphological changes were observed. At ambient temperature and a pressure of 3.5 MPa, the scattering curve, as evidenced by the appearance of a Bragg peak at q=0.12 Å<sup>-1</sup> (corresponding to a bilayer of lecithin), was consistent with a coexistence of the mixed vesicle I phase and the lamellar phase. The coexistence remained up to a pressure of 51.8 MPa, where the phase became lamellar. Guinier analysis of scattering data as a function of temperature revealed that the vesicles remained spherical with the average size increasing as the temperature was reduced from 40 to 15 °C. The stability of the mixed vesicle phase with respect to the lamellar phase as a function of pressure and temperature will be discussed in terms of Helfrich's model of the curvature elastic free energy.

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#### **B2P.05**

PHYSICAL INVESTIGATIONS INTO TWO CHROMONIC DYES USED IN CANCER THERAPY. A.D.Stennett, H.F.Gleeson, M.R.Dickinson, and N.B.McKeown\*. Dept. of Physics and Astronomy, University of Manchester, M13 9PL. \*Dept. of Chemistry, University of Manchester, M13 9PL

We present results from an investigation into two substituted phthalocyanines known to show lyotropic liquid crystal phases. The physical properties of these compounds as measured using polarising optical microscopy, X-ray diffraction, UV-Vis spectroscopy and Raman spectroscopy are presented.

This detailed examination of the liquid crystalline and optical properties of the drug are ultimately to be used to identify its behaviour in simulated biological systems. This should enable us to understand better whether there is a connection between the action of the drug against cancer and its liquid crystalline properties.

#### **B2P.06**

ROLE OF THE DIFFUSIONAL FACTORS IN ACTIVITY OF ENZYME IMMOBILIZED BY BILAYER PHOSPHOLIPID VESICLES, Yu. E. Shapiro\* and A. V. Smirnova, A.V.Bogatsky Physico-Chemical Institute of the Ukrainian Academy of Sciences, Odessa, 270080, Ukraine.

The kinetic parameters for enzymatic hydrolysis of classic substrate, p-nitrophenyl acetate, in presence of  $\alpha$ -chymotrypsin immobilized, and non-immobilized by phospholipid bilayer liposomes are essentially differed. The immobilization of  $\alpha$ -chymotrypsin tends to increase of the value of Michaelis constant by a factor of 1.5, and to decrease of the value of maximum rate by a factor of 1.8. These distinctions are conditioned by diffusional factors arised with immobilization of enzyme. Indeed, the value of appropriate Michaelis constant calculated according to the diffusion coefficient for components of reaction medium is practically agree with experimental constant for  $\alpha$ -chymotrypsin immobilized by phospholipid vesicles. The dimensions of empty liposomes, and liposomes with immobilized enzyme for dimension control were determined by use of the methods of light-scattering.

<sup>\*</sup>Supported by Grant 2.2.1/18 of Ukranian State Committee on Sciences & Technology.

A LIQUID CRYSTAL MODEL OF THE DNA MOLECULE AND ITS APPLICATION TO THE MELTING PROBLEM, <u>V.B.Nemtsov</u>, Belarussian State Technological University, 13a, Sverdlova Str., Minsk, 220 630, Belarus.

A DNA molecule is considered as an one-dimensional chiral smectic liquid crystal in which the smectic layers are generated by the nitrous base pairs (adenine, thymine, guanine and cytosine). These bases lie perpendicular to a "pitch" axis, about which they rotate as one moves along it. The heat of melting (unwinding) of DNA molecule is estimated on the basis of this model and by using of the previously developed theory of the new caloric effect under the deformation of the cholesteric liquid crystals [1]. The entropy of melting is expressed in the terms of the twisting rigidity, the helical pitch and the temperature coefficient of expansion. The calculated heat of unwinding of the DNA molecule is of the order of the corresponding experimental amount. The theory of caloric effect is extended to the case of the bending and twisting of the DNA molecules.

[1] V.B.Nemtsov, Theor.Matem.Phys. (Moscow), 14, 262 (1973); Ukrain. Phys. Journ. (Kiev), 37, 378 (1992); V.B.Nemtsov and V.S. Vikhrenko, Mol. Cryst. Liq. Cryst., 262, 569 (1995).

**B2P.08** 

CaCO<sub>3</sub> CRYSTALS AND LIQUID CRYSTALS IN SOME ANIMALS, Xuehong Xu\*, Q. Lu, C. Tang, H. He, School of Life Science, Wuhan University, Wuhan 430072, P. R. CHINA

CaCO<sub>3</sub> crystals are existing extensively in animal bodies in three forms of crystal structure i.e. calcite, aragonite and vaterite. Our investigations have showed that CaCO<sub>3</sub> aragonite or vaterite forming is related to liquid crystal forming (LC) in the same position of animal organ. During chick embryo developing, the LC droplets appeared in yolk sac at the 2nd day of incubation and the quantity increased gradually and came to a maximum at the 7th day. At this time, CaCO<sub>3</sub> vaterite could be detected. Its quantity increased gradually. The yolk sac of 7-10 days old was filled with CaCO<sub>3</sub> vaterite granules proved conclusively by XRD. In the inner-ear of P seud oscidena polyactis, statoconia of CaCO<sub>3</sub> aragonite [1] is surrounded by the lymph with LC. In the certain period of pearl development of freshwater clam, pearl crystal of CaCO<sub>3</sub> aragonite existed in the media of pearl sac or mantle cavity, where the LC droplets also appeared in quantities. The phenomena imply that CaCO<sub>3</sub> aragonite in these animals is related to LC.

[1] X. Xu, H. He, et al, Acta Hydrobiologica Sinica, 19(3), 240(1995).

\* Supported by NSF Grant of P. R. China and Test & Analysis Program of Chinese Academy.

**B2P.09** 

LIQUID CRYSTALS IN SOME ANIMALS, <u>Xuehong Xu\*</u>, Q. Lu, H. He, L. Chao, and X. Wu, School of Life Science, Wuhan University, Wuhan 430072, P. R. CHINA.

We have investigated the liquid (LCs) crystals in the development of embryo of animal since 1978. The recent studies show that LC also can been found in other period of animal life. The results are

Animals	Tissue or cell	LC droplet existing period	Texture	Lamellar structure by freeze-etching	Thickness by SAXS(Å)
chick, pheasant, Taihe fowl, duck, quail, pigeon	hepacyte, yolk	development and prestage of postdevelopment	Maltese-cross droplet	concentric	37. 1, 37. 4, 37. 6, 36. 8 37. 8, 38. 4 (in liver)
gecko, tortoise	hepacyte	as above	as above	as above	
snakeheaded fish	hepacyte	reproductive	as above	as above	
Chinese honey bee, Italian honey bee	trophocyte in fat body	metamorphosis	center-empity Maltese-cross droplet	AUTER-CARCERTRIC	<b>44.</b> 1

<sup>\*</sup> Supported by NSF Grand of China and YOUTH Program of Wuhan Government.

### B2P

#### **B2P.10**

CONFORMATIONAL FLUCTUATIONS FOR MOLECULES OF DNA TYPE, V.L. Golo and <u>E.I. Kats</u>, Landau Institute for Theoretical Physics, Russian Academy of Sciences, Kosygin str. 2, Moscow GSP-1 117940, Russia.

We derive a functional Fokker-Planck equation [1], [2] for the conformational fluctuations of long linear molecules of DNA type, calculate the correlation function for fluctuations of the local frame, and show that it is essentially the response function of a molecule under the action of an external force. For the important specific case of the molecule conformation being a helix, we demonstrate that the contribution to the energy of molecule generated by fluctuations of its form, results in generating a rotating torque, a kind of Casimir's force [3], depending on the pitch of the helix.

- [1] V.L. Golo and E.I. Kats, Pisma ZhETF 60, 666 (1994).
- [2] V.L. Golo and E.I. Kats, ZhETF 78, 482 (1994).
- [3] H.B. Casimir, Proc. Kon. Ned. Akad., 51, 793 (1948).

#### **B2P.11**

THE LIQUID CRYSTALS OF BLOOD PLASMA IN METABOLIC DISORDER, V.V.Zaitsev, N.B.Zaitseva, N.V.Kaledenkova, N.V.Usoltseva, Molecular Physics Chair, Ivanovo State University, Ermaca str. 39, 153025, Ivanovo, Russia.

Monomer-polymer bases were obtained by plasmochemical method, glow discharge was used in Kr with addition of organic monomer. While structure of the blood plasma in healthy and sick peaple was investigated on orienting bases, pseudoisotropic texture—was immediately shown in crossed Nicols, where, with an ×106 magnification, one could see a correct 120°-angle change in transmission of light, if the microscope was rotating. Polarization microscopy made evident the following textures, registered in the patients with myocardial infarction: irregular filamenous ones (the angle is not 120°), fanned, small spherolytes, spherolytes, large spherolytes, small dendrites, dendrites, acicular crystals. Fanned textures and pseudoisotropic structures with changes in the transmission of light [<120°] are found in the blood plasma for the first time with plasmochemical orientating coating. The systematical investigations of textures (more than 50 patients with myocardial infarction and donors) under temperatures 20, 36, 40 °C allows to obtain the time dependencies (0-120 hours) of dimensions (30-600 mm) for different metabolic disorders.

#### **B2P.12**

SYNTHESIS, CHARACTERIZATION AND BIO-ASSAY OF CHOLESTERIC LIQUID CRYSTALS (Cholesteryl Linoleate/Oleate), R.M. Lalanto, R.M. Padilla, L.G. Cada, Z.B. Domingo, Liquid Crystals Laboratory, National Institute of Physics, Institute of Chemistry, University of the Philippines, Diliman, 1101 Quezon City, Philippines.

Cholesteryl linoleate and cholesteryl oleate were synthesized in a two-step esterification process by preparing an acid chloride from linoleic and oleic acid then reacting it with cholesterol in the presence of a catalyst. Purification of the esters was done by recrystallization and column chromatography. Purity of the synthetic esters was evaluated by thin layer chromatography. Samples were characterized using Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry and Optical Microscopy and evaluated with reference to SIGMA cholesteryl linoleate/oleate. Bio-assay of samples in an in-vivo Micronucleus Test reduced incidence of micronucleated polychromatic erythrocytes by 71.19% for the synthetic cholesteryl linoleate and 79.30% for the SIGMA sample. An in-vitro Cell Culture Test revealed potency of an optimum concentration of cholesteryl linoleate at 100 µL to inhibit the growth of Tetrahymena thermophila after 12 hours. The effectivity of the synthetic cholesteryl linoleate in inhibiting the growth of Tetrahymena thermophila was determined to be 106% in reference to a positive control of SIGMA sample.

DETERMINATION OF THE LIQUID CRYSTALLINE PROPERTIES OF ERYTHROCYTE MEMBRANES, M.dela Merced, L.G. Cada\*, R. Matias\* and Z.B. Domingo, Liquid Crystals Laboratory, National Institute of Physics, Institute of Chemistry\*, Dept. of Molecular Biology and Biotechnology\*, University of the Philippines, Diliman, 1101 Quezon City, Philippines.

A study has been made on the mesomorphic properties of membrane preparations from normal and abnormal human red blood cells using a variety of physical techniques such as Fourier-Transform Infrared Spectroscopy (FTIR), Optical Microscopy, and Differential Scanning Calorimetry (DSC). FTIR spectra of air-dried normal and abnormal ghosts confirmed that both are of the same composition. Characteristic textures of the lyotropic neat phase were observed in normal erythrocyte ghosts and may exhibit the nematic phase similar to those observed in thermotropic LCs. DSC thermograms of normal ghosts showed that these samples undergo phase transitions from a crystalline gel to smectic to nematic to a homogeneous solution at the temperature range of ~10°C - 70°C. At the physiological temperatures (~35°C -37°C), the membranes exhibited the lamellar smectic phase further lending support to the fluid-mosaic model of cell membranes. Similar tests performed on membranes of thallasemic (abnormal) red blood cells yielded no results that are similar and comparable to the liquid crystalline behavior of normal membranes.

**B2P.14** 

DYNAMICS OF A LYOTROPIC CUBIC PHASE, M. Clerc<sup>(1)</sup>, Y. Hendrikx<sup>(1)</sup>, and B. Farago<sup>(2)</sup>, <sup>(1)</sup>Laboratoire de Physique des Solides, Bât. 510, Université Paris-Sud, 91405 Orsay cedex, France; <sup>(2)</sup>Institut Laue Langevin, 38042 Grenoble cedex, France.

We study the cubic phase made of the non-ionic surfactant  $C_{12}(EO)_6$  in presence of water (1,2). The 3D periodic structure of this phase is characterized by the space group Ia3d. This structure corresponds to a centred cubic phase where the surfactant molecules build two identical 3D periodic interwoven labyrinths separated from each other by a continuous water medium. We present recent results obtained at ILL on spectrometer IN11. Our experiments show for the first time, the dynamical character of the fluctuations observed in the investigated cubic phase. Therefore spin echo measurement have been performed on a single crystal ( $\sim 0.1 \text{ cm}^3$ ). The time dependent diffusion function S(q,t) has been measured for different scattering vectors q. For q vectors which do not correspond to Bragg peaks, the neutrons are scattered according to a quasi-elastic process and the associated S(q,t) function decreases which a characteristic time of 10 ns. The dynamical fluctuations are probably particular deformation modes of the labyrinths. The nature of the modes has to be identified.

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**B2P.15** 

LANDAU-BRAZOVSKII THEORY OF THE GYROID PHASE, <u>V.E.Podneks</u> and I.W. Hamley, School of Chemistry, University of Leeds, Leeds, LS2 9JT U.K. Permanent address: Oil and Gas Research Institute, Moscow, Russia.

The "gyroid" phase of Ia3d symmetry is the most commonly observed bicontinuous phase in lyotropic liquid crystals, and has also been observed for block copolymer melts [1-3]. We present mean field Landau theory that accounts for its stability, and theory that incorporates composition fluctuations. Allowance for fluctuations leads to a renormalization of the quartic terms in the Landau free energy, in particular the mixed term from the first two harmonic order parameters. This leads to the theoretical prediction of a direct transition from the isotropic - gyroid phase, in agreement with experiments [3].

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MICROSTRUCTURES IN AN OIL-in-WATER MICROEMULSION: A NMR SELF-DIFFUSION STUDY

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We present the accurate measurements of water, oil and surfactant self-diffusion coefficients made in the microemulsion phase of the pentaethylene glycol dodecyl ether  $(C_{12}E_5)$ , water and decane. Fourier Transform NMR self-diffusion experiments provided insights into solution microstructure via investigation of the long-range mobility of the different components. The self-diffusion coefficients of oil and surfactant molecules have been measured using the pulsed gradient stimulated-echo NMR experiment<sup>1</sup>. We have analysed the microstructure of three microemulsion phases obtained with different surfactant-to-oil volume ratios. Particular attention was focused at the phase boundary where the microemulsions consist of normal oil swollen micelles in equilibrium with excess oil. Increasing the temperature, a micellar growing was supported by self-diffusion results and finally a bicontinuos phase was found.

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#### **B2P.17**

LIQUID CRYSTALLINE CHARACTER OF AMPHIPHILIC QUATERNARY AMMONIUM POLYACRYLATES, D. Tsiourvas, M. Arkas and C. M. Paleos, Institute of Physical Chemistry, NCSR "Demokritos", 15310 Aghia Paraskevi, Attikis, Greece

It has been established that quaternary ammonium halides with long alkyl chains exhibit thermotropic liquid crystalline character [1]. The liquid crystalline behaviour of these salts is affected, as expected, by the nature of the counter ions, the length of the lipophilic chain and the functionalization of the quaternary moiety [2]. In the present work the simple halide counter ion of a series of quaternaries is replaced by a polyacrylate anion [3] of average molecular weight 5000 and the liquid crystalline properties of these polymeric quaternaries were studied. The smectic liquid crystalline phases exhibited by these materials were differentiated from their analogous monomeric counterparts bearing the same functional groups i.e. CN, OH and COOH attached on the cationic center by a spacer of three methylene groups.

C. M. Paleos, Mol. Cryst. Liq. Cryst. 243, 159 (1994).
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#### **B2P.18**

DECARBOXYLATION OF 6-NITROBENZISOXAZOLE-3-CARBOXYLIC ACID THROUGH PHASE TRANSITION IN LYOTROPIC LIQUID CRYSTALS, <u>Y.K.Yarovoy</u>, L.Campbell and M.M.Labes \*, Temple University, Chemistry Department, Philadelphia, PA 19122

Kinetics of the spontaneous unimolecular reaction of 6-nitrobenzisoxazole-3-carboxylic acid decarboxylation have been studied in the nematic and isotropic lyophases formed by anionic, cationic and nonionic surfactants: sodium decyl sulfate (SDS), myristyltrimethylammonium bromide (MTAB) and 5-oxyethylene lauryl ether ( $C_{12}EO_5$ ) respectively. Without surfactants the reaction goes equally slow in both acidic (pH 4.0) and alkaline (pH 9.0-11.0) water solutions, with the reaction rate ~0.7x10<sup>-5</sup> s<sup>-1</sup> (at 25°C). Anionic SDS has no catalyzing effect on the reaction. Cationic MTAB significantly accelerates the reaction (~100 times at pH 9.0 and ~ 80 times at pH 4.0; 25 °C) in all phases: isotropic, lamellar or cylindrical nematic. Nonionic  $C_{12}E_5$  is the only surfactant which shows a catalyzing effect dependent on the type of the lyophase. The reaction goes ~1.5 times faster in the lamellar as compared to the isotropic phase.

<sup>\*</sup>Supported by NSF Grant DMR-93-12634.

INVESTIGATING THE EFFECTS OF POLAR ORGANIC SOLVENTS ON PERFLUORINATED SURFACTANTS, Neville Boden, Richard Harding, SOMS Centre. Leeds University, Leeds, LS2 9JT, UK, Ken W Jolly, Scott J Thomsen Dept. of Chemistry & Biochemistry, Massey University, Palmerstone North, New Zealand.

The phase behaviour of perfluorinated surfactants has been determined in a range of nonaqueous solvents. It is found that liquid crystal phase formation is suppresed. The behaviour of these surfactants dissolved in water/non-aqueos solvent mixtures has also been investigated. The roles of counter-ion binding and interfacial tension on aggregation stability. and consequently phase behaviour is examined.

**B2P.20** 

LYOMESOMORPHISM OF FLAT TETRAPALLADIUM ORGANYLS: ON THE LENGTH OF THEIR SIDE CHAINS VERSUS LENGTH OF SOLVENT MOLECULES, N. Usol'tseva, K. Praefcke\*, B. Heinrich#, V. Vatagin, and A. Bronnikova, Liquid Crystal Laboratory, Ivanovo State University, C.I.S.-153025 Ivanovo, Russia, \*Institute of Organic Chemistry, Technische Universitat Berlin, D-10623 Berlin, Germany, #I.P.C.M.S.- Groupe des Materiaux Organiques, F-67037 Strasbourg Cedex, France.

For the first time, we could show now that the occurrence of two nematic phases side by side in binary mixtures of such organyls with linear alkanes [1] is strictly dependent on the ratio of the number of methylene units in both the side chains and alkanes used as solvent.

Results obtained by polarizing microscopy and FT IR spectroscopy will be presented and discussed in detail.

[1] N. Usol'tseva, K. Praefcke, D. Singer, and B. Gundogan, Liq. Cryst., 16, 601 (1994).

Supported by the EU Contract No. CHRX-CT 93-0163 Supplementary Aggreement CIPDCT 940607 (Brussels, Belgium) and by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich Sfb 335 "Anisotrope Fluide", project C6 and projects Pr 116/18-1 and 436 Rus 113/31).

**B2P.21** 

LYOTROPIC PHASE BEHAVIOUR OF DI-PALLADIUM ORGANYLS IN APOLAR OR-GANIC SOLVENTS, N. Usol'tseva<sup>††</sup>, K. Praefcke<sup>‡</sup>, P. Espinet<sup>‡</sup>, <u>D. Blunk</u><sup>‡</sup> and M. J. Baena<sup>‡</sup> Liquid Crystal Laboratory, Ivanovo State University, CIS-153025 Ivanovo, Russia, <sup>‡</sup>Institute of Organic Chemistry, Technische Universität Berlin, D-10623 Berlin, Germany, ¶Quimica Inorganica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain In order to gain a better insight on the influence of molecular geometry on the lyotropic mesomorphism [1-3]

we have investigated the behaviour of both linear [3] and twin-like [4] di-palladium organyls in solvents mentioned in the title. Whereas in ternary systems of the linear mesogen with an electron acceptor like TNF and an apolar solvent a nematic and a columnar hexgonal mesophase are observed, the twin-like Pd-complex displays lyotropic behaviour only without TNF. Two ways of influence of apolar organic solvents on the lyomesophase formation of the different di-palladium organyls will be discussed:

• the formation of lyomesophases possessing a similar type of molecular arrangement in both, the lyoand the thermotropic mesophases,

• the fascinating induction of new types of supramolecular packing in the lyotropic state, resulting in a different architecture of the mesophases.

N. Usol'tseva, K. Praefcke, D. Singer, B. Gündogan, Liq. Cryst., 1994, 16, 601 and 617.

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M. J. Baena, Ph.D. Thesis, University of Valladolid (Spain), 1993.

LYOMESOMORPHISM OF PHTHALOCYANINE ETHERS IN APOLAR ORGANIC SOLVENTS\*, N. Usol'tseva. V. Bykova, G. Ananjeva, A. Semeikin, and T. Karmanova, Liquid Crystal Laboratory, Ivanovo State University, 153025 Ivanovo, Russia.

Previously, we investigated the lyotropic behaviour of anionic macrocyclic compounds in aqueous solutions [1]. In order to study the lyotropic phase behaviour of *hydrophobic* phthalocyanine derivatives, various metal (copper & nickel) complexes of octa(dodecyloxy)phthalocyanine (1, 2) and tetra(dodecylthio)phthalocyanine (3) have been synthesized. In contact preparations with aromatic or aliphatic solvents, e.g. benzene, cyclic or linear alkans, all these compounds show lyotropic properties. Usually, Schlieren, non-geometrical or "herring-bone" textures were observed. On the basis of phase diagrams of the binary systems composed of 1, 2 or 3 with pentadecane the influence of the mesogene structure on the lyomesomorphism will be discussed.

[1] a) N.Usol'tseva, Lyotropic Liquid Crystals: Chemical and Supermolecular Structure (IvGU, Ivanovo, 1994), 91; b) N. Usol'tseva, V. Bykova, G. Ananjeva, and V. Maizlish, Bull. Acad. Sci. Russia, Phys. ser. 59, 49 (1995).

\*Supported by the EU PECO Contract ERBCIPDCT940607 (Brussels, Belgium) and by the International Programme of GoskomVuz (Moscow, Russia).

#### **B2P.23**

LYOTROPIC POLYMORPHISM IN OXO-VANADIUM COMPLEXES, S. Sherry Zhu and Timothy M. Swager\*, Department of Chemistry, University of Pennsylvania, Philadelphia, PA. 19104

New surfactants incorporating paramagnetic oxo-vanadium centers I, II, III, and IV are reported, which display high stability in aqueous environments and lyotropic behavior. Compounds I and II exhibit lamellar phases in binary (H2O/Surfactant) systems. I only displays lyotropic behavior at elevated temperatures. The ternary phase behavior (H2O/Decanol/Surfactant) of II was studied in detail and added decanol stabilized the lamellar phase to low concentrations (=6%) of II. Compounds III and IV with their larger head volume relative to tail size don't display binary lamellar phases but display lyotropic liquid crystalline behavior in ternary systems. Compound III was studied in detail and was found to display both hexagonal and lamellar phases. The lamellar phase is stable over a very large region and was found to change its optical sign with the composition.

#### **B2P.24**

BANDED TEXTURE INDUCED BY AN ELECTRIC FIELD IN LYOTROPIC LIQUID CRYSTALS, K. Monzen, D. Fujita, H. Hiraoka, Y. Uematsu, and M. Date\*, Tokyo Institute of Polytechnics, Atsugi, Japan. \*The Institute of Physical and Chemical Research, Wako, Japan.

Using polarization microscopy, the formation of transient banded textures in the liquid crystalline solution of poly( $\gamma$ -benzyl L-glutamate),PBLG, that had been applied in-plane D.C. and A.C. electric fields was investigated. The striped bands perpendicular to the direction of the electric field were observed under applying an electric field. The images depended on time were recorded by video camera and then analyzed. The dynamics of director-reorientation was followed by the measurement of optical transmittance for the sample sandwiched between crossed polarizers. The reproducible optical response to the square wave in low frequency region was recognized well. The dependencies of the band spacing and the reorientation rate of director on the field strength, the sample thickness and temperature were quantitatively investigated.

STABILITY OF BINARY LYOTROPIC LC MIXTURES, R. van Roij and <u>B. M. Mulder</u>, FOM Institute for Atomic and Molecular Physics, Kruislaan 407, NL-1098 SJ Amsterdam, The Netherlands

We have derived a general criterion for the stability of binary mixtures described in terms of effective two-particle interactions. Application to elongated rod-like hard particles show that some mixtures of particles with different diameters may phase separate in the isotropic phase, before the transition density to the nematic phase is reached. The mechanism is entirely analogous to the depletion mechanism that causes phase separation in mixtures of unequal sized colloids [1]. The same mechanism also predicts phase separation at high enough densities in the nematic phase in the presence of perfect alignment, albeit that now the lengths of the particles need to be sufficiently different. A reanalysis of the solution of the Onsager model at high densities also allows a verification of the prediction that freely rotating rods of different lengths will phase separate at densities corresponding to the isotropic-nematic transition, in which case the instability is driven by orientational entropy differences [2].

[1] H. N. W. Lekkerkerker and A. Stroobants Physica A 195 387 (1993)

[2] G. J. Vroege and H. N. W. Lekkerkerker J. Phys. Chem. 97 3601 (1993)

**B2P.26** 

SMECTIC MESOPHASE IN THE MIXTURES OF TRISTEARIN WITH DIMETHYL SULFOXIDE, A P Divya, M S Madhava, D Revannasiddaiah and R Somashekar, Department of Physics, University of Mysore, Manasagangotri, Mysore 570006, India.

Mixtures of Tristearin with Dimethyl sulfoxide (DMS) from 20% to 80% show non-aqueous lyotropic liquid crystalline phase with the range of mesomorphism varying between 50 to 80 C. Optical and X-ray studies indicate smectic like structure in these mixtures.

**B2P.27** 

ISOTROPIC-HEXAGONAL LYOTROPIC LIQUID CRYSTAL PHASE TRANSITION IN THE SODIUM LAURYL SULFATE (SLS) SYSTEM, R.Itri, C.V.Teixeira and L.Q.Amaral, Department of Applied Physics, Institute of Physics of University of Sao Paulo, CP 66318, 05389-970, Brazil

We have studied concentrated micellar solutions of sodium dodecyl (lauryl) sulfate in water by small angle x-ray scattering which presents an Isotropic (I) - Hexagonal (H $\alpha$ ) phase transition by increasing SLS molar concentration (at Mw= 24 ,Mw=water:SLS molar ratio). Further it has also been found that by increasing decanol amount, at a fix Mw=45.2, the system undergoes I -> H $\alpha$  ->Nematic Cilindric (Nc) -> Nematic Discotic (Nd) phase transition. It is a very interesting point since the theoretically predicted phase sequence is I ->Nc ->H $\alpha$ . Analysis of the small angle scattering curves of the I phases is performed through the modeling of the product of the micellar form factor and intermicellar interference function. From these results we discuss the effect of decanol in changing the way the H $\alpha$  phase is approached in the binary and the ternary system.

supported by FAPESP/Brazil

NATURE OF  $L_{\beta} \rightarrow P_{\beta'}$  PRETRANSITION IN LECITHIN / WATER AND LECITHIN / LYSOLECITHIN / WATER MULTIBILAYERS: A  $^2$ H-NMR AND CALORIMETRIC STUDY, A.Checchetti $^1$ , G.Chidichimo $^1$ , A.Golemme $^1$ , D.Grasso $^2$ , D.Imbardelli $^1$ , C.La Rosa $^2$ , F.P.Nicoletta $^1$  and P. Westerman $^3$ ,  $^1$ Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy;  $^2$ Dipartimento di Chimica, Università di Catania, via A. Doria 8, 95125 Catania, Italy;  $^3$ Department of Biochemistry and Molecular Pathology, Northeastern Ohio Universities' College of Medicine, P.O. Box 95, Rootsown, Ohio 44272, U.S.A.

The nature of the  $L_{\beta}$  (gel)  $\rightarrow$   $P_{\beta'}$  (ripple) pretransition in aqueous dispersions of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and the effect of incorporation of 1-palmitoyl-sn-glycero-3-phosphocholine (PLPC) on the structure of the  $P_{\beta'}$  mesophase have been studied by deuterium nuclear magnetic resonance (<sup>2</sup>H-NMR), differential scanning calorimetry (DSC) and scanning dilatometry (SD). For samples containing 34 weight percent of water and a weight percent of PLPC between 0 and 15, a pretransition of decreasing intensity with increasing PLPC concentration was observed by DSC. The pretransition disappears at 15 weight percent PLPC. The presence of a non-zero asymmetry parameter in the <sup>2</sup>H-NMR spectra of the lipid mixtures incorporating a <sup>2</sup>H-labelled DPPC suggests that the rippled structure which exists in the  $P_{\beta'}$  mesophase may also be present in the  $L_{\beta}$  gel phase.

#### **B2P.29**

MODULATING THE PHASE BEHAVIOUR OF LYOTROPIC DISCOTIC LIQUID CRYSTALS BY INCORPORATION OF A THIRD COMPONENT, Neville Boden, Richard J. Bushby and John F. Hubbard, SOMS Centre, University of Leeds, Leeds, England, LS2 9JT, UK.

The discotic amphiphile TP6EO2M, in aqueous solution, undergoes self-assembly into columnar aggregates, in turn undergoing self-organisation on longer length scales to produce a rich variety of mesophases [1]. Adding a third component, which is an electron deficient material, causes the dopant to be incorporated between the molecules in the aggregated stacks. This in turn can lead to the stabilisation of mesophases already present as well as the potential to introduce specific properties such as chirality.

[1] N. Boden, R. J. Bushby, C. Hardy, and F. Sixl, Chem. Phys. Lett., 123, 359 (1986).

#### **B2P.30**

## STRUCTURAL INVESTIGATIONS ON NEMATIC AND LAMELLAR LYOTROPICS BY MEANS OF CHIRALITY INDUCTION

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The structures of lyotropic nematic as well as of lamellar liquid crystals are still questionable. For the latter phase competing models have been proposed, i) the smooth bilayer, ii) the defective bilayer, iii) positionally ordered micelles. Also for some 'nematic' systems hints to long-range positional order have been reported in the literature. We have examined these structural aspects by adding small amounts of chiral dopants to nematic and lamellar phases; the resulting phase chirality has been studied in the nematic as well as at the continuous or discontinuous chiral nematic to lamellar phase transitions by temperature dependent pitch measurements; positional ordering was checked by small angle x-ray scattering. Further evidence of structural differences between the 'nematic' phases of the investigated CsPFO/water and SLS/decanol/water systems has been found.

THE INFLUENCE OF THE MOLECULAR STRUCTURE OF DI- AND TETRAPHENYL PORPHIN DERIVATIVES ON LYOMESOMORPHISM, <u>V.Bykova</u>, N.Usol'tseva, G.Ananjeva, A.Semeikin, T.Karmanova, Liquid Crystals Laboratory, Ivanovo State University, Ivanovo, 153025, Russia.

The synthesis and ivestigation of the manifestation of lyotropic liquid crystalline properties depending on the molecular structure of organic compounds have been traditionally connected with plank-like amphiphylic compounds. In recent years lyotropic mesomorphism of compounds containing disc-like molecules has been successfully investigated [1,2]. The fact that thermotropic mesomorphism was revealed in molecules of mixed form: with a disc-like central fragment and two symmetric substituents has led us to synthesize di- and tetraphenil derivatives of porphin [3] with the object of forming lyotropic mesophases in water-ammonia systems and organic solvents. On the strength of the data of polarization microscopy and spectrum analysis it has been shown that the formation of lyomesophases is affected both by the structure of synthesized ligands and by the nature of metal complexes and pH solvent.

[1] N.Usol'tseva, V.Bykova at all. Mol.Cryst. 1992. Vol.215. P.89.

[2] V.Bykova, N.Usoltseva at all. Mol.Cryst.Liq.Cryst. Hungary, 1995. Vol.265. P.651.

[3] В.Быкова, Н.Усольцква и др. Изв.АН Серия физическая. 1995. Т.59. N 3. С.56.

**B2P.32** 

LYOTROPE PHASE BEHAVIOUR OF PHTHALOCYANINE DERIVATIVES IN APOLAR ORGANIC SOLVENTS, N.Usol'tseva, V.Bykova, A.Semeikin, G.Ananjeva, A.Smirnova, V.Negrimovski, Liquid Crystals Laboratory, Ivanovo State University, Ivanovo, 153025, Russia.

With the object of studying lyotropic mesomorphism of macrocyclic compounds with symmetric substitution of alkyl chains copper and nickel complexes of octadodecyloxyphthalocyanine  $(\underline{1},\underline{2})$  and copper complex of tetraalkylthiophthalocyanine  $(\underline{3})$  have been synthesized and their mesomorphism has been investigated.

In binary systems with aromatic and aliphatic solvents, e.g. benzene, cyclohexene, or linear alkane all these compounds displayed lyotropic liquid crystalline phases, characterized by Shlieren-texture, non-geometrical or "herring bone"-texture.

On the basis of the of data of the phase diagrams composed by binary systems of phthalocyanine derivatives (1.2 or 3)/pentadecane we have discussed the influence of the change of the mesogen structure on the lyomesophase formation.

**B2P.33** 

EXPERIMENTAL INVESTIGATION OF LYOTROPIC LIQUID—CRYSTALLINE (LLC) SYSTEM STRUCTURE PHOTORESPONSE TO THE LOW—INTENSITY OPTICAL IRRADIATION EXPOSURE EXCLUDING THERMAL DESTRUCTIVE EFFECTS, R. I. Mints, D. B. Berg, Laboratory of Applied Biophysics, Urals State Technical University, Yekaterinburg, 620002, RUSSIA.

Structure effect of the low-intensity wide-band optical irradiation in infrared region (IR) on the smectic (lamellar) mesophase of the lipid LLC was investigated according to the following scheme: parameters estimation, computer experiment, native (physical) realization, analytical comparison of the model and physical experimental results. Transmitted through the sample IR irradiation was used to get the information about the structure of the lipid and water components of LLC. Sample concentration metastability and heterogeneity was due to the preparation technique. Water contents in the LLC was: a)  $H_2O - 10\%$ ; b)  $H_2O - 5\%$  and  $D_2O - 5\%$ . The range of 4000–1500 cm<sup>-1</sup> corresponding to the water molecules OH and OD and lipid polar head -C=O, -P=O, -C=O-C, -C=O-C, -C=O-C, alent vibrations was investigated [1]. Correlating changes of the absorption peak maximums numbers and their intensities during the exposure process (1-10<sup>2</sup> minutes) due to the lipid polar head conformation changes and water "bonding" degree were observed. It is shown that photostimulated relaxation of the LLC concentration metastable states results in structure changes of "lipid-water" complexes and increase of the LLC heterogeneity size scale.

[1] D. Berg, and V. Chukanov, Mol. Mat., 4, 327 (1994).

MEASUREMENT OF THE SPLAY-BEND ELASTIC CONSTANT IN LYOTROPIC FERRONEMATIC LIQUID CRYSTAL: THE INFLUENCE OF THE BOUNDING SURFACES, S. Fontanini, A. Alexe-Ionescu, G. Barbero and A.M. Figueiredo Neto, Instituto de Física da Universidade de São Paulo, Caixa Postal 66318, CEP 05389-970, São Paulo, SP, Brasil.

We report an experimental investigation devoted to analyze the influence of a ferrofluid on the surface properties for lyotropic liquid crystals doped with magnetic particles. The bulk orientation of the director versus the temperature was measured, for two different ferrofluid concentrations. The theoretical analysis shows that when it is near the nematic-isotropic transition, the mechanical model for the temperature surface transition works reasonably well. Important deviations have been observed at a low temperature region, near the nematic-lamellar transition. We propose a simple phenomenological extension for the mechanical model, taking into account different contributions to the surface energy. Not only does the free energy per unit surface depend on the coupling between the ferrofluid grains and the lamellar layer in the bounding surfaces but also on the ferrofluid and the micelles. The measured effective splay-bend elastic constant is positive and of the order of 1. It decreases with increasing amounts of ferrofluid in the bounding surfaces. The difference between the bulk tilt angle and the easy angle at the surface increases for increasing amounts of ferrofluid in the sample. Financial support: FAPESP and CNPq.

PERIODIC DISTORTIONS IN LYOTROPIC NEMATIC CALAMITIC LIQUID CRYSTALS, M. Simões, Departamento de Física, Universidade Estadual de Londrina, Campus Universitário, 86051-970, Londrina (PR), Brazil, A. J. Palangana and L. R. Evangelista, Departamento de Física, Universidade Estadual de Maringá, Av.Colombo, 5790, 87020-900 Maringá (PR), Brazil.

A theoretical tool to determine the dependence of the wavelength of the periodic structures on the applied magnetic field in lyotropic liquid crystals in the nematic calamitic phase is proposed[1]. It is assumed that the periodic structure experimentally found can be represented by a sequence of walls. Our calculations indicate that in order to describe the measured behavior of the system above the Frederick's threshold the interaction between these walls must be taken into account. The strength of these interactions and the ratio between the bend and twist elastic constants are also determined.

[1] Submitted for publication in the Physical Review E.

#### **B2P.36**

THE EFFECTS OF POLYETHYLENE OXIDE ON CURVATURE ELASTICITY OF MICELLAR NEMATIC CESIUM PERFLUOROOCTANOATE WATER MIXTURES, S. S. Pak and A. Saupe\*, Orion Electric Co., Ltd., Gumi, Kyungbuk 730-030, Korea, \*Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

This study focuses on the effect of polyethylene oxide (PEO) on the elastic properties of micellar liquid crystals formed by the cesium perfluorooctanoate (CsPFO) water system. Measurements were made on samples with 49 wt % CsPFO. We used PEO with molecular weights of 100,000 and 300,000 and prepared samples with a CsPFO concentration of 49 wt % and replaced water partially by small amounts of PEO. The weight fractions of water replaced by the polymer were 0.25, 0.60 and 1.0 wt %. The goal was to determine the temperature and concentration dependence of accessible macroscopic properties, birefringence, spaly and bend elasticity. These properties were obtained by analyzing the static optical response of surface aligned films in magnetic fields. Accordingly, the replacement of water by the polymer affects in particular the properties that diverge with the smectic coherence length. The splay elasticity is not changed by the polymer, indicating that the curvature elastic properties are influenced only indirectly through the change of smectic short range order.

<sup>\*</sup>Supported by NSF Grant DMR 89-03453.

DETERMINATION OF ELASTIC CONSTANTS AND ROTATIONAL VISCOSITY OF DISCOTIC MICELLAR LIQUID CRYSTAL BY CONDUCTIVITY MEASUREMENTS, G. Hillig, J. Bajc, A. Saupe, Max-Planck-Society Research Group Liquid Crystalline Systems, Halle, Germany, Department of Physics, University of Liubljana, Liubljana, Slovenia

Mixtures of CsPFO/ $H_2O$  = 49/51 wt% exhibit a lamellar phase and a nematic phase, consisting of disk-like micelles. Due to the dissociation of the ionic surfactant, the lyotropic mesophases have a high electric conductivity. The conduction anisotropy depends on the liquid crystalline order of the micelles and temperature [1]. Conductivity measurements were performed in a cylindrical capillary (R = 1,25 mm) with homeotropic boundary conditions. The configuration of the director field of the nematic phase is determined by the surface anchoring and the bend and splay elastic constants. In equilibrium an escape structure is assumed [2]. We studied the electric conductance as a function of a magnetic field (1-8 kGauss) applied parallel to the capillary axis, statically and dynamically. The measurements were analysed to determine the elastic constants  $k_{11}$  and  $k_{33}$  and rotational viscosity  $\gamma_1$ . It was not possible to obtain reliable values for both elastic constants independently. Near the nematic-lamellar phase transition we observe as expected an increase of  $k_{33}$  and  $\gamma_1$ .

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**B2P.38** 

ORIENTATIONAL DIFFUSIVITIES MEASURED BY PHOTON CORRELATION FOR A DISK-LIKE NEMATIC (N<sub>D</sub>) PHASE OF A NEW LYOTROPIC LIQUID CRYSTAL SYSTEM M.B. Lacerda Santos<sup>a</sup>, A.M. Figueiredo Neto band E.A. Andreoli b,

<sup>a</sup> Departamento de Física, Universidade de Brasília, 70910-900 Brasília, DF, Brazil

<sup>b</sup> Instituto de Física, Universidade de São Paulo, 01498-970 São Paulo, Brazil

Using a light-beating technique we have measured the damping time of thermal fluctuations of the nematic director for the disk-like  $(N_D)$  phase of the rather new lyotropic system [1] K-laurate/ decylamonium hydrochloride,  $H_2O$ . The scattering geometry was appropriate to determine the splay and twist diffusivities. A similar measurement formerly made [2] for the  $N_D$  phase of an older system, K-laurate/ decanol/  $D_2O$  yielded to a large deviation between the values of these two diffusivities, which was interpreted in terms of backflow. The new measurements reported here confirm the applicability of the model in spite of the physico-chemical differences of the two micellar systems.

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[2] M.B. Lacerda Santos, Y. Galerne and G. Durand, J. Phys. Paris, 46, 933 (1985).

**B2P.39** 

FLOW BIREFRINGENCE OF LYOTROPIC POLYAMIDES AND POLYETHERS IN ACID SOLUTION, T.V.Filippova, I.N.Shtennikova, Institute of Macromolecular Componds, Russian Academy of Sciences, St.Petersburg, Bolshoi pr.31, 199004, Russia.

For many years we have investigated molecular properties of aromatic polyamides in delute acid solutions [1]. This work is made for the investigation of the influence of the monomer unit structure on the conformational properties of the new lyotropic poly (biphenil-sulfone terephtalamide) (PPhSTPhA):

$$-NH$$
 NHCO CO  $-$ 

Flow birefringence and intrinsic viscosity method is used for characterization in wide molecular weight range such PPhSTPhA conformational properties as equilibrium rigidity (Kuhn segment), optical anisotropy of monomer unit, rotatory diffusion coefficient. All these properties of PPhSTPhA are compeared with those of other before investigated polyamides and polyethers which are used as fibremaking materials.

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DYNAMIC LIGHT SCATTERING OF A LYOTROPIC LIQUID CRYSTAL LAMELLAR PHASE AND A SPONGE PHASE, <u>J. Oizumi</u>, Y. Kimura, K. Ito, and R. Hayakawa, Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Nonionic surfactants  $C_{12}E_5$  in aqueous solutions aggregate to form a lyotropic liquid crystal lamellar  $(L_{\alpha})$  phase. The layer separation of  $L_{\alpha}$  phase increases up to nearly half of the wavelength of light with the decrease of the surfactant concentration C. This highly swollen  $L_{\alpha}$  phase is stabilized by a steric repulsion between the layers. With a further decrease of C, the aggregation of surfactants changes to a sponge  $(L_3)$  phase composed of randomly aligned layers. Dynamic light scattering (DLS) measurement of the highly swollen  $L_{\alpha}$  phase showed that there existed two modes which were supposed to be originated from the baroclinic mode [1]. In the present study, we have investigated the DLS of the  $L_{\alpha}$  and  $L_3$  phases by changing C. It is found that the elastic constant  $k_C$  of  $L_{\alpha}$  phase is of the order of the thermal energy  $k_B T$ , and increases with increasing C. The size of randomly aligned layers in the  $L_3$  phase is also estimated.

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#### **B2P.41**

LIQUID CRYSTALLINE AND SURFACTANT PROPERTIES OF ALKYL PYRIDINIUM SALTS, Daniel P. Jackson and B. M. Fung, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019-0370, U. S. A.

Several new alkyl pyridinium salts, namely 1-n-alkyl-4-cyanopyridinium bromides with alkyl chains containing 14, 16, and 18 carbons, were synthesized, and their mesomorphic and micellar properties were studied. For compounds with 16 and 18 carbons in the alkyl chain, a theromotropic smectic A phase is present. Each compound was mixed with the corresponding 1-n-alkyl-4-methylpyridinium bromide in a variety of mole fractions, and the phase transition behavior of the mixtures was studied. The compounds also behave as surfactants in dilute aqueous solutions. Therefore, the Krafft temperature and the critical micelle concentration of each compound were determined.

#### **B2P.42**

A STATISTICAL MODEL FOR HYPERMICELLAR AGGREGATION. V.A. Lobaskin and V.K. Pershin\*. Physics Dept., Cheliabinsk State University, Br. Kashirinykh str. 129, 454136 Cheliabinsk, Russia.

Hypermicellar aggregation in diluted micellar systems is studied in the limits of a statistical model, which is a modification of lattice theories of solutions. Within the framework of our model the free energy of a solution is a sum of configurational entropy determined for solute particles, potential energy of intermicellar interaction and gravitational potential energy of micelles. An original technique based on methods of the graph theory is suggested for calculation of cluster entropy. The potential energy of the aggregates is calculated as the cohesion energy for neighboring micelles according to the approach developed in [1]. The excess free energy of aggregation is calculated in the approximation of loose hypermicellar clusters with different types of architecture. The temperature is determined, above which the micellar system becomes unstable with respect to aggregation. It is found that the transition temperature depends on micelle volume fraction. It is shown that gravitational effects are negligible in free dispersed phase but become considerable for large aggregates near the transition point. Micellar systems containing loose sea-weed-like clusters are found to exhibit non-universal pre-transitional behaviour.

[1] V.A. Lobaskin and V.K. Pershin. *Mol. Cryst. Liq. Cryst.* 260, 585 (1995); *Mol. Materials* 5, 29 (1995). \*The work is supported by RBRF Grant No.95-02-05974a

NUCLEAR MAGNETIC RELAXATION NEAR THE NEMATIC-TO-ISOTROPIC TRANSITION IN MICELLAR SYSTEMS. <u>V.M. Chernov</u>, R.I. Valeev, Department of Physics, Cheliabinsk State University, Br. Kashirinykh str. 129, 454136 Cheliabinsk, Russia

Using the NMR <sup>19</sup>F method, nuclear transversal magnetization is studied over the nematic-to-isotropic transition region for aqueous micellar solutions of caesium perfluorononanoate. Transversal magnetization decay (TMD) appears to be one-component in both nematic and isotropic phases but two-component in the two-phase region. Componental composition of the TMD changes rapidly near the low-temperature border of the coexistence region and slowly near the high-temperature border. Long exposition at fixed temperature leads to spatial phase separation of the micellar system: the isotropic phase floats while the nematic one sinks. It is argued that this fact is due to a difference in micellar concentrations in the two phases.

**B2P.44** 

MONTE CARLO SIMULATION OF A DILUTED MICELLAR SOLUTION. V.A. Lobaskin and N.A. Smirnov, Physics Dept. Chelyabinsk State University, 454136 Chelyabinsk, Russia

Using the Monte Carlo method and Metropolis technique we have studied stability of a diluted nonionic micellar solution with respect to phase separation. Within our model micelles have been considered as interacting hard spheres. The potential of intermicellar interaction has been taken to be a sum of the steric repulsion between carbohydrate micelle cores, the dispersion attraction and temperature dependent hydration repulsion [1]. As the result of the simulation we have found that there exists a lower temperature border, above which micelles aggregate into extended clusters. We have studied structure and dynamics of these clusters at different temperatures and concentrations. We have also calculated the Kirkwood-Buff integrals and estimated the potential of mean force, the osmotic compressibility and the second virial coefficient for micelles in the solution of nonionic surfactant n-dodecyl octaoxyethylene glycol monoether in water.

[1] V.A. Lobaskin and V.K. Pershin, Mol. Cryst. Liq. Cryst. 260, 585 (1995); Mol. Materials 5, 29 (1995)

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ANALYSIS OF X-RAY DIFFRACTION INTENSITIES OF A MESOGENIC MIXTURE EXHIBITING INDUCED SMECTIC PHASE, M.K. Das and R. Paul, Department of Physics, North Bengal University, Siliguri, Darjeeling, Pin-734430, W.B., India.

Mixture of 5CB and ME6O.5 exhibits induced smectic phase over the certain composition range [1]. From x-ray diffraction, we have calculated the average intermolecular lateral distance (D) between the molecules and smectic layer thickness (d) for different mole fraction (x) of 5CB. At T=35°C the D value shows a maximum near x=0.5, whereas both density and layer thickness [1] show a reverse trend i.e. minimum near x=0.5. This behaviour of D explains why the density of the mesogen decreases even when the layer thickness is also decreasing. Assuming molecules to be arranged in a tetragonal primitive lattice, whose long axis is the average molecular length and other axes are equal to experimental D value, we have calculated the density at different compositions of this mixture. Our calculated values agree reasonally well with the experimental values.

[1] M.K. Das and R. Paul, Phase Trans., 46, 185(1994), Phase Trans., 48, 255(1994).

**B3P.02** 

ELECTROPHYSICAL PROPERTIES OF LIQUID CRUSTAL IN DYNAMICS OF X-RAY IRRADIATION IN THE RANGE OF TEMPERATURES OF PHASE TRANSITIONS.B.S. Saburov Tajik Agricultural University 734017,146 Rudaki pr., Dushanbe, Republik of Tajikistan

In the paper the results of X-ray irradiation on electrophysical properties of liquid crustals (LC) in the range of temperatures of phase transition smectic phase(SLC) — solid crustal (SC) are given. It is established that doses of X-ray irradiation used (up to  $4.2 \mathrm{Gr/s}$ ) do not induce destruction of liquid crystals that manifests itself in conservation after irradiation of all the temperatures of phuse transitions and temperature intervals of mesophase existence. It is shown that additional conductivity

 $46 \pm G_{\rho} - G_{o}$  (where  $G_{\rho}$ ,  $G_{o}$  are conductivities of samples induced by X-ray irradiation and free from it) arising in the range if temperatures of phase transition SLC-SC, similar to intrinsic conductivity, has peak value and is negative in sigh(4620). In addition peaks of intrinsic and additional conductivities are level with each other on tamperature scale. Decrease of conductivity  $G_{o}$  and ap pearance of negative  $G_{o}$  in the range of temperatures of phase transition SLC-SC in dynamics of X-ray irradiation can be explained by phenomenon of recombination of charges generated under irradiation with carriers of natural current.

**B3P.03** 

PHYSICAL AND MOLECULAR PROPERTIES OF THREE MESOGENIC PHENYL CYCLOHEXANE COMPOUNDS, A. Nath, P.Mandal and S. Paul, Department of Physics, University of North Bengal, Siliguri - 734430, INDIA.

Small angle X-ray diffraction studies have been performed at different temperatures on the magnetically oriented samples of two alkenyl phenyl cyclohexane non-polar compounds and one alkyl phenyl cyclohexane compound with a polar terminal group having nematic phase only. Densities and optical birefringes have also been determined. Orientational order parameters are calculated both from X-ray and optical data. From the measured values of apparent molecular length we find that the polar compound forms dimers, for the non-polar compound no dimer formation has been observed. Some anomalous behaviour was observed in the optical and density studies of the non-polar compounds. Order parameters determined from X-ray data also show some anomalous behaviour, although the photographs show that the phases throughout the temperatures ranges are nematic. We try to explain the anomaly on the basis of physical and molecular properties.



X-RAY SCATTERING STUDIES ON TWO NEMATOGENIC p-ALKYLPHENYL-2-CHLORO- 4-(p-ALKYLBENZOILOXY)-BENZOATES, <u>Pranab Sarkar</u>, Parimal Sarkar, Sukla Paul and Pradip Mandal, Physics Department, North Bengal University, Darjeeling-734430, INDIA.

The compounds, p-octylphenyl-2-chloro-4-(p-heptylbenzoyloxy)-benzoate and p-pentylphenyl-2-chloro-4-(p-pentylbenzoyloxy)-benzoate, show nematic phase in the temperature ranges 34 to 100°C and 39 to 122°C respectively. Marble textures were observed under a crossed polarizing microscope, however, near N-I transition schlieren textures were observed. Both of them exhibit supercooled nematic phase below room temperature. Moreover, mixture of equal weight of them forms nematic phase even at room temperature. Small angle X-ray scattering studies of magnetically aligned sample of the first compound have been done in the entire nematic range. The average intermolecular distance, calculated from outer diffraction maxima, is found to be ~5.2 Å. The apparent molecular length, obtained from the inner diffraction maxima, is found to be ~32.9 Å. Temperature dependence of these parameters will be discussed. Stereo-model length of the molecule in all *trans*-configuration is 33 Å, so the molecules are in most extended form also in nematic phase. Calculation of orientational order parameters <P2> and <P4>, from the angular intensity distribution of the outer ring, is in progress. X-ray studies on the second and on the mixtures of different compositions of the two compounds will also be reported.

#### **B3P.05**

STRUCTURE OF LIQUID CRYSTALLINE PHASE IN HEXAKIS(4-(4'-ALKYLOXY)BIPHENOXYCYCLOTRIPHOSPHAZENE, Keiichi Moriya and Anne Marie Levelutt, Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido Gifu 501-11, Japan †Laboratoire de Physique de Solides, Universite Paris-Sud, Orsay 51405, France

X-ray measurements of hexakis(4-(4'-alkyloxy)biphenoxy)cyclotriphosphazenes [PN(OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>OC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>]<sub>3</sub>(HACP, n=7-9) confirm the previous mesophase identification. The apparent molecular length measured in the mesophase compares to twice the length of an alkyloxybiphenyl side groups. In addition to the usual features of the nematic and smectic diffraction patterns, a second ring characterizing the molecular lateral array is observed. This ring corresponds to a (x $\sqrt{3}$ ) superlattice of the side group array. In the nematic phase, a staggered array of the molecules along the director have been observed. This array presists locally in the smectic phase forming linear defects parallel to the director. These specific features both originate from the peculiar shape of the cyclotriphosphazenes. [1]

[1] Anne Marie Levelut and Keiichi Moriya, Liq. Crystals, in press.

#### **B3P.06**

THE REMARKABLE PHASE BEHAVIOUR OF SOME *n*-ALKYL 1-*O*-β-D-FRUCTOPYRANOSIDES, JW Goodby<sup>a</sup>, JA Haley<sup>a</sup>, G Mackenzie<sup>a</sup>, R Pindak<sup>b</sup>, <u>MJ Watson</u><sup>a</sup>, D Plusquellec<sup>c</sup> and V Ferrières<sup>c</sup>; <sup>a</sup>School of Chemistry, University of Hull, Hull, Hu6 7RX, UK; <sup>b</sup>Bell Laboratories, Lucent Technologies, 600 Mountain Ave, Murray Hill, NJ 07974, USA; <sup>c</sup>Laboratoire de Synthèses et Activations de Biomolécules, Ecole Nationale Supérieure de Chimie, Ave du Général Leclerc, 35700 Rennes, France.

Monoalkyl substitution in carbohydrate systems is known to affect the melting behaviour of sugars and support the introduction of thermotropic liquid-crystalline phases. Similarly, the inclusion of a relatively long aliphatic chain in the molecular stucture affects the formation of lyotropic liquid crystal phases. Here, the liquid-crystalline properties of a family of monoalkylated fructopyranosides are described. Additionally, the thermal behaviour of the materials is discussed in terms of simple molecular models of geometrically optimised structures, and the resulting degree of hydrogen bonding possible for the various materials. Finally, X-ray diffraction techniques on selected materials are used to evaluate the structure of the thermotropic liquid crystal phases.

X-RAY INVESTIGATIONS ON LINEAR AND BRANCHED ALKYLENE AMINE DERIVATIVES R. Festag, M. Wittenberg, J.H. Wendorff, Fachbereich Physikalische Chemie und Wissenschaftliches Zentrum für Materialforschung, Philipps-Universität Marburg, D-35032 Marburg, Germany U. Stebani, G. Lattermann, Makromolekulare Chemie I, Universität Bayreuth, D-95440 Bayreuth

Oligoalkylene amine derivatives with 3,4- bis(alkoxy)benzoyl substituents show different ordered mesophase structures. Lamellar, hexagonal, rectangular and even cubic mesophase formation was detected by X-ray scattering [1, 2]. This behavior can not be explained in classical terms of anisometric molecular or supramolecular units but phase separation between polar centers and apolar side chains might be the driving force for mesophase formation. Structural variations introduced (length of the alkylene amine backbone or branching) to influence the conformational flexibility of the backbone.

[1] U.Stebani, G.Lattermann, R.Festag, M.Wittenberg, J.H.Wendorff, J.Mater.Chem., 1995, 5(12), 2247

[2] U.Stebani, Dissertation, Bayreuth 1995

**B3P.08** 

STRUCTURAL PROPERTIES OF LIQUID CRYSTAL MIXTURES BASED ON THE HOMOLOGOUS SERIES OF ALKOXYPHENYL ALKOXY BENZOATES D.Ž. Obadović<sup>†</sup>, L. Bata<sup>‡</sup>, T. Tóth Katona<sup>‡</sup> and K. Fodor-Csorba<sup>‡</sup>

† Faculty of Natural Sciences, Institute for Physics, Trg D. Obradovića 4., Novi Sad, Yugoslavia, ‡ Res. Inst. for Solid State Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B.49, Hungary Binary and ternary mixtures were prepared on the members of the homologous series of 4-n-alkoxyphenyl 4'-n-alkoxy benzoates. The 4'-n-heptyloxy-phenyl-4-n-octyloxy benzoate and 4'-n-heptyloxy-phenyl-4-n-decyloxy benzoate have the phase transition temperatures (in °C) Cr 62  $S_C$  69 N 88 I and Cr 67  $S_C$  79  $S_A$  82 N 89 I, respectively. Their eutectic mixture have the phase sequence Cr 51  $S_C$  76  $S_A$  78 N 89 I on heating and I 90 N 79  $S_A$  76.5  $S_C$  33  $S_B$  31  $C_T$  on cooling. With the chiral additive of (S)-(1-methylheptyl)-1,1'-4'-1"-terphyenyl-1,4"-dicarboxilate we got a ferroelectric compound with the phase transitions of Cr 48  $S_{C(I)}^*$  55  $S_{C(II)}^*$  73  $S_A^*$  75 Ch 80 I. The physical and electro-optical properties such as spontaneous polarization, tilt angle and switching time were studied. In this paper we present the temperature dependence of the layer spacings for all smectic liquid crystalline phases and the average intermolecular distances measured by X-ray diffraction on non-oriented samples. The smectic layer spacings for ternary, binary and single components have the values 31.79Å, 30.8Å, 30.3Å and 24.6Å, respectively.

**B3P.09** 

X-RAY STUDY AND MOLECULAR MODELLING OF THE MESOGEN 4-PENTYLCYCLO HEXYL-4-(4-PROPYLCARBOXYL)BENZOATE, Golam Mostafa\*, Anuradha Mukhopadhyay\*, Siddhartha Ray\* \* Department of Solid State Physics, Indian Association for The Cultivation of Science, Jadavpur, Calcutta 700 032. \* Department of Physics, Jadavpur University, Jadavpur, Calcutta 700 032.

X-ray diffraction studies of 4-pentylcyclohexyl-4-(4-propylcyclohexyl)benzoate has been conducted at various temperatures. The above sample is known to undergo the following phase transitions:

Solid 42 C Sm1 72 C Sm2 128 C nematic 193 C isotropic

On the basis of X-ray diffraction and texture studies the Sm1 and Sm2 phases have been identified to be the SmE and SmB phases respectively. The molecular lengths / apparent layer thickness and average intermolecular distances in the various phases have been obtained from X-ray diffraction photographs at various temperatures. The order parameter in the SmB phase has also been calculated and a comparison of the experimental and theoretical values made as a function of temperature.

In order to get an estimate of the molecular structure and charge density in the minimum energy configuration, AM1 calculations have been done. This is being used in molecular dynamics simulation to study the bulk phase liquid crystalline behaviour of the mesogen.

STRUCTURE OF PCH4, <u>I.H.Ibrahim\*</u>, H. Paulus\*\*, and W. Haase\*\*, \*Department of Physics, Faculty of Science, Alexandria University, Alexandria, Egypt, \*\*Institut für Physikalische Chemie, TH Darmstadt, D-64283 Darmstadt, Germany.

The crystal and molecular structure of the mesogenic trans-4-nbutyl-(4-cyanophenyl)-cyclohexane (PCH4) has been determined using single crystal x-ray diffraction data. The crystals belong to the monoclinic system with space group P2,/c, a=17.006(6), b=5.764(2), c=15.526(5)Å,  $\beta$ = 96.73(1)°, Z=4.The structure of PCH4 has been solved by direct methods and refined to R-value of 0.0484 for 1779 observed reflections. All the molecules accur in involves crystal packing extended form. The their centrosymmetric head-to-tail pairing of molecules, so that individual molecular dipoles are opposed with cyano-cyano overlapping.

#### **B3P.11**

REINVESTIGATION OF MESOMORPHIC PROPERTIES OF 4,4'-DIALKYLBIPHENYL. NEW ORTOGONAL PHASES. K.Czupryński, R.Dąbrowski, Military University of Technology, 01-489 Warsaw, Poland J.Przedmojski, Warsaw University of Technology, 01-662 Warsaw, Poland

The phase transitions in a few members of homologous series of 4,4'-dialkylbiphenyl were reinvestigated. The existence of a different smectic E phase in the same compounds was confirmed by thermomictroscopic, X-rays and DSC studies [1,2]. The miscibility results evidently show that three different phases of the E type must exist.

n=5 m=5 Cr 25.1 - E 46.1 E' 47.1 B <sub>cryst.</sub> 52.3	Iso
11-5 111-5 Ci 25.1 - 15 40.1 2 111 cryst	
n=5 m=6 Cr ? E" 11.7 E 41.7 E' 42.6 B <sub>cryet</sub> 53.7	Iso
n=6 m=6 Cr 25.1 E" 46.1 E 47.1 - B <sub>cryst.</sub> 52.3	Iso
n=0 in=0 cr 25.1 D 40.1 D 40.5	Iso
11-0 111-7 C1 1 E 27:7 E 30:2 -cryst.	Iso
n=7 m=7 Cr ? E" 19.5 E 35.1 - B <sub>cryst.</sub> 61.0	150

X-ray difractograms will be shown.

[1] K.Czupryński, Liq.Cryst., 16, 399 (1994)

[2] K. Czupryński, J. Przedmojski, J. Baran, Mol. Cryst. Liq. Cryst., 260, 435 (1995)

#### **B3P.12**

A NEW WEAKLY-BIREFRINGENT HIGH-TEMPERATURE MESOPHASE IN TETRACATENAR COMPOUNDS, G.Pelzl, I.Letko, S.Diele, A. Saupe\* and W.Weissflog\*, Institut für Physikalische Chemie, Martin-Luther-Universität, 06108 Halle / S., Germany, \*Max-Planck-Arbeitsgruppe "Flüssigkristalline Systeme", D-06108 Halle/S., Germany

In some six -or seven-ring double swallow-tailed compounds a new high-temperature mesophase (here designated as  $M_X$ ) could be observed in different phase sequences:  $\Phi_{ob} \Phi_h M_X$  Is;  $S_C \Phi_{ob} M_X$  Is or  $S_C$  cubic  $M_X$  Is. Generally this new phase appears as a mosaic texture. On very slow cooling large homogeneous domains can be obtained which are distinguished by shaded grey tones between crossed polarizers. The birefringence was found be very weak  $(3x10^{-3})$ . With falling temperature within the domains series of black lines (homeotropic or isotropic) arise which are more or less parallel to the direction of the maximum refractive index  $n_Y$ . On further cooling these lines can be intersected by another sets of parallel lines giving rise to unusual and exotic textures. According to preliminary X-ray investigations the  $M_X$  phase can be characterized by a three - dimensional lattice superimposed upon a short - range liquid order of the centres of mass. The high viscosity and the delayed growth of the  $M_X$  phase point to a mesophase similar to the cubic phase only distinguished by a weak anisotropy.

STRUCTURAL STUDIES OF SYMMETRIC LIQUID CRYSTAL DIMERS PR Alapati, RW Date, GR Luckhurst and JM Seddon, Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, UK

Liquid crystal dimers in which two Schiffs base groups are linked by a flexible spacer have been shown to exhibit a rich smectic polymorphism. Although certain of the transitional properties show the anticipated large odd-even effect our main concern is with the structural properties of the smectic phases. These properties are exemplified by the behaviour of the odd and even dimers,  $\alpha$ ,  $\omega$ -bis(4-nonylanilinebenzylidene-4'-oxy)pentane (9.050.9) and its hexane analogue (9.060.9). Both dimers form smectic A, C and F phases with strong  $S_A$ -I and  $S_F$ - $S_C$  transitions. ESR spectroscopy has been used to study the orientational order in monodomain smectic phases and the tilt angle in the  $S_C$  phase. Somewhat unexpectedly, the tilt angle in the smectic C phase of both dimers is small and does not exceed 9° even at the end of the range. For coexistent  $S_C$  and  $S_F$  phases there is a difference of about 15° in the tilt angle. These findings are consistent with the results of X-ray diffraction measurements on powder samples. The implications of these results for the packing of odd and even dimers with their quite different molecular shapes within the smectic phases are profound.

[1] R W Date, C T Imrie, G R Luckhurst and J M Seddon, Liq. Crystals, 12, 203 (1992).

**B3P.14** 

CRYSTAL STRUCTURE OF 4-ISOTHIOCYANATOPHENYL 4-PENTYLBICYCLO [2,2,2] OCT-ANE-1-CARBOXYLATE, M.A. Sridhar, N.K. Lokanath, D. Revannasiddaiah, and <u>J Shashidhara Prasad</u>, Department of Studies in Physics, University of Mysore Manasagangothri, Mysore 570 006, INDIA.

The title compound is a mesogen which exhibits nematic phase. The interesting feature of this compound is the presence of an eight membered ring as the rigid core. Crystal structure studies of such compounds is very meagre. The solid to nematic transition temperature is  $74.5^{\circ}$ C and the clearing point is  $113.5^{\circ}$ C. The title compound crystallizes in the space group  $P\overline{1}$ . The structure was solved using SHELXS-86[1] and refined using SHELXL-93[2]. The final residual factor is R1 = 0.069 for  $I > 2\sigma(I)$ . There are four molecules in the asymmetric unit. The molecular packing along two directions shows imbrication, whereas down c layering is also observed. It may be surmised that the material may exhibit smectic phase under varying physical conditions.

[1] G.M. Sheldrick, Acta Crystallogr. A46, 467 (1990).

[2] G.M. Sheldrick, SHELXL-93—CSRP, University of Göttingen, Germany.

**B3P.15** 

THE INFLUENCE OF THE INCLUSION OF A NON-LINEAR MACROCYCLE IN CALAMITIC LIQUID CRYSTALS: SYNTHESIS AND PHASE BEHAVIOUR Rachel P. Tuffin, Georg H. Mehl, Kenneth J. Toyne, John W. Goodby, School of Chemistry, University of Hull, Hull HU6 7RX, England

We report the results of the synthesis and the investigation for the phase behaviour of a series of materials based on the macrocycle 1,7-diaza 4,10,13-oxacyclopentadecane. By positioning the macrocycle between mesogenic units, materials with a tilt in their core region could be generated. Keeping the mesogenic units constant and varying the length of the terminal alkyl chain allowed for a comparative study of the influence of the size of the molecules on the formation of tilted smectic phases. With increasing size of the molecules a decrease of the crystallisation temperature and the injection and stabilisation of an additional tilted phase was observed. The liquid-crystalline morphology was investigated by mixing experiments, optical polarising microscopy, differential scanning calorimetry and X-ray diffraction.



HIGH- RESOLUTION X-RAY DIFFRACTION OF A CONJUGATED PHENYL-ACETYLENE MACROCYCLE, <u>0. Mindyuk</u>, P. A. Heiney, and S. S. Ghosh, Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA, U.S.A.; J. Nelson and J. Moore, Chemistry Department, University of Illinois at Urbana-Champaign, IL, U.S.A..

We have used high-resolution x-ray diffraction to study the structure of a liquid crystalline conjugated phenylacetylene macrocycle (PAM) [1]. Columnar mesophases based on a these rigid, ring-shaped molecules are of interest because of their potential organization into supramolecular channels. The PAM studied forms a columnar liquid crystal with a distorted hexagonal lattice. We present a detailed structural analysis of our data.

[1] J.Zhang and J. Moore, J. Am. Chem. Soc., 116, 2655 (1994) and references therein. Supported by NSF DMR MRL 92-20668 and DMR 93-15341 (Penn) and NSF grant CHE 94-96105 (Illinois).

#### **B3P.17**

X-RAY STUDY OF THE MESOPHASE-MESOPHASE TRANSITION OF OCTAALKYLOXY-ORTHOCYCLOPHANES, S.Dai, N. Spielberg, Physics Depart., Kent State U., Kent, OH, 44242, USA; H.Zimmermann, Max Planck Inst.f.Med.Forsch., AG Molekülkristalle, Jahnstrasse 29, 6900 Heidelberg, Germany

Previous optical microscope and x-ray studies [1] of the mesomorphic octaether derivatives of cyclotetraveratrylene, CTTV-I-n, where n is the number of carbon atoms per ether chain, have shown that there are two columnar mesophases for 9 < n < 16. No heat of transition was detected for the transition between the two mesophases. Powder x-ray data for the higher temperature phase was indexed on a two dimensional hexagonal unit cell and for the lower temperature phase on a two dimensional centered rectangular unit cell. For n=13, the transition between the two phases took place over a wide temperature range (20° C). We find this wide transition region is a third mesophase, with an oblique lattice intermediate between the other two. The upper boundary of this phase marks symmetry breaking of the hexagonal lattice by the appearance of a unit cell having  $\gamma=120^\circ$ , but with  $a\neq b$ . With decreasing temperature, b is essentially constant while a and  $\gamma$  increase until the lower phase boundary is reached, at which point  $2a \cos \gamma = b$ , as is characteristic of the primitive cell for the two dimensional centered rectangular lattice. Similar behavior is observed for the compound n=14, but not for n=12 or n=15, for which the "transition region", if it exists, is too narrow for our apparatus.

[1] N.Spielberg, M.Sarkar, Z.Luz, R.Poupko, J.Billard, H.Zimmermann, 1993, Liq. Crystals, 15, 311.

## **B3P.18**

NEUTRON SCATTERING STUDIES ON REENTRANT NEMATIC PHASE, M.Mitra, R.Paul\*, S.K.Paranjpe\* and K.Usha Deniz\*, Dept. of Physics, Bangabasi Morning College, 19 Scott Lane, Calcutta-9,India; \*Dept. of Physics, North Bengal University, Darjeeling, India; \*Solid State Physics Division, BARC, Trombay, Bombay, India.

The aim of this work is to find out how the short range ordering changes as we go from normal nematic to reentrant nematic phase. The binary mixtures of 6OCB and 8OCB exhibits reentrant behaviour over a narrow range of compositions. The characterizations of the mixtures have been done. We have taken a mixture having 6OCB of 27.12% by weight over 8OCB. The transition temperatures of the phase sequences are as follows:

Solid (24C) RN (32.8C) SmA (41.7C) N (77.9C) Iso.

Neutron Scattering studies have been done by using the Profile Analysis Spectrometer at Dhruva Nuclear Reactor, BARC, Bombay [1]. We have fitted the intensity values I(Q) with a Lorentzian function as;  $I(Q) = I_b(Q) + c/[k^2 + (Q-Q_0)^2]$ , with  $I_b(Q) = a + bQ$  and a, b, c, k and  $Q_0$  are the fitting parameters. The correlation length ( $\xi$ ) can be obtained from the fitted values of k. We have used the relation  $D = 1.117 \times 2\pi/Q_0$  to calculate intermolecular distance (D) from the fitted values of  $Q_0$ . The results are discussed.

S. K. Paranjpe and Y. D. Dande, Pramana-J.Phys. 32, 793 (1989).
 This work is supported by I.U.C. for D.A.E. Facilities.

ELASTIC AND QUASIELASTIC NEUTRON SCATTERING ON LIQUID CRYSTALS GY. TÖRÖK, K. FODOR-CSORBA, LROSTA Research Institute for Solid State Physics, H-1521 Budapest P.O.Box 49, Hungary

We have investigated the structure and dynamics of liquid crystal compound using neutron scattering facilities of Budapest Neutron Centre. We have made a series of neutron scattering experiments on solid and mesogenic phase of ethoxy-benzil-butylaniline (EBBA) and (-2-methyl-buthyl)-4'-n-heptyl-biphenyl-4-carboxylate (7BEF5) liquid crystals to interpret the molecular dynamics. We have carried out a powder diffraction measurement on 7BEF5 to get information about the solid phase structure at ambient temperature t≈20°C. The quasielastic measurement on EBBA at t=20°C resulted a line broadening even in solid phase in range of 10µeV. The quasielastic measurement on 7BEF5 at q=0.213Å-1 gave not any broadening of quasielastic peak, but give a broadening at different q=0.666 Å-1 in range of 10µeV. This behaviour probably is connected with different flexibility of molecules that leads to the different kind of phase transition of EBBA and 7BEF5.

**B3P.20** 

BILAYER PACKING OF THE NEMATOGENE MOLECULES IN THE INDUCED SMECTIC A PHASE, Yu. E. Shapiro, and A. Yu. Boytsov, A.V.Bogatsky Physico-Chemical Istitute of the Ukrainian Academy of Sciences, Odessa, 270080, Ukraine.

Induced enantiotropic smectic A phases arise usually in the mixtures of two amphyphilic nematogenes. A steady existence of the SmA phase in the wide area of temperatures and compositions on the phase chart is the peculiarity of these systems. With aid of  $^{13}$ C-NMR spectroscopy we have discovered a dynamic intermolecular associates in structure of such SmA phase induced by mixing of two nematogenes 4-pentyloxy-4"-cyanobiphenyl (1, high polar) and hexyloxyphenylic ester of the nonylbenzoic acid (2, low polar). These associates are connected by means of dipole-dipole interaction between CO-and CN-groups, and dispension forces between complementary packed aryl fragments. An analysis of the  $^{13}$ C chemical shifts and of the  $^{13}$ C spin-lattice relaxation times,  $T_1$ , variations confirms the bilayer model of the molecular packing for induced SmA phase. By formation of such associates the carbonyl group of compound 2 continually exchange the partner because of lateral diffusion. Moreover the COOAr aromatic ring is situated normally to the layer plane between two biphenyl aromatic rings of compound 1. This one facilitates the co-operative rotation of the aromatic rings of interacting molecules within bilayer.

**B3P.21** 

THE ULTRASONIC INVESTIGATION OF A MAGNETIC FIELD INDUCED STRUCTURAL CHANGES OF A SMECTIC C PHASE, <u>A.S.Kashitsyn</u>\*, V.A.Balandin and S.V.Pasechnik, \*Ivanovo State University, PLLC, 153025, Ermak St., 39, Ivanovo, Moscow State Academy of Instrument and Informatics, 107846, Strominka 20, Moscow, Russia.

By means of an ultrasonic method we have studied the changes of a structure of a smectic C induced by magnetic fields  $\bf B$  and  $\bf B_o$ . The field of the induction  $\bf B_o$  was used for an orientation of the a nematic phase of liquid crystal sample and this field was fixed during a cooling the sample from a nematic phase through a smectic C phase [1]. We used the field of the induction  $\bf B$  to change the structure of a smectic C. The values both of  $\bf B$  and  $\bf B_o$  could be change to induce the structural changes of a smectic C phase. These changes produced the variations of an ultrasonic attenuation coefficient. The different models of a smectic C phase we applied to explain the experimental dependencies of an attenuation coefficient on induction  $\bf B$  and  $\bf B_o$ .

[1] S.Pasechnik, V.Balandin, A. Kashitsyn, Mol.Cryst.Liq.Cryst.192, 89(1990). Supported by ISF Grant MIT-300.

A PLASTIC COLUMNAR DISCOTIC PHASE, B. Glüsen, A. Kettner, J.H. Wendorff, Fachbereich Physikalische Chemie and Wissenschaftliches Zentrum für Materialforschung, Philipps-Universität Marburg, D-35032 Marburg, Germany

We report a novel discotic phase with three dimensional crystal like registry of orderd columns in a hexagonal lattice but with rotation of the disc molecules within the columns. The phase has features in common with the plastic crystalline state [1]. This so called Dhp-phase has been observed in several symmetrically and asymmetrically substituted triphenylene derivatives. Such highly ordered columnar phases display high charge-carrier mobilities in photoconductivity experiments [2]. The structure of the mesophases were characterized by X-ray diffraction, the dynamics by dielectric relaxation spectroscopy.

[1] B. Glüsen, W. Heitz, A. Kettner, J.H. Wendorff, Liq. Cryst. 1996 in press
[2] J. Simmerer et al. submitted to Adv. Materials
Supported by the Fonds der Chemischen Industrie and the DFG (SFB 383)

#### **B3P.24**

MOESSBAUER SPECTROSCOPY OF METALLOMESOGENS: PARAMAGNETIC COMPLEXES, V.Ya.Rochev. V.G.Bekeshev, Yu.G.Galyametdinov, N.N.Savvateev, F.Wagner<sup>+</sup>, G. Grosse<sup>+</sup>, Institute of Chemical Physics RAS, Moscow, 117334, Russia; <sup>+</sup> - Department of Physics, Technical University of Munich, D-85748, Garching, Germany.

Earlier we have studied the structure and properties of nematic diamagnetic ferrocene containing mesogens [1]. The use of them as a chelating ligands allows to syntesize the new type of metal containing liquid crystals: polynuclear coordination compounds <sup>57</sup>FeL<sub>2</sub>Cl ( where L - ligand ), which are paramagnetics and show together with nematic also smectic polymorphism. Using the Moessbauer, ESR, X-ray spectroscopy and the magnetic susceptibility measurements, the molecular structure of these complexes was established and their coordination, dynamical and magnetic properties were studied. In particular it was shown that these complexes contain two different kinds of high-spin Fe<sup>3+</sup> forming the isolated and chlorine-bonded chain complex units. According to Moessbauer and magnetic susceptibility data the transition from paramagnetic to antiferromagnetic state for these complexes take place in a wide temperature interval between 140 and 4.2K. The complete magnetic ordering and the disappearance of Moessbauer spectra relaxation forms was observed only at 4,2K in external magnetic field of 6T.

[1] V.Ya.Rochev and V.G.Bekeshev, Mol.Cryst.Liq.Cryst., 265, 9, (1995).

#### **B3P.25**

HERRING BONE ORDER IN HEXATIC B PHASE? EPR STUDY OF LIMITED MOLECULAR ROTATION IN ORTHOGONAL SMECTICS, <u>I.Bikchantaev</u>, J.Szydlowska, D.Pociecha, A.Krowczynski, E. Gorecka, Warsaw Univer., Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland; Rus. Acad. Science, Kazan, Russia.

The EPR studies of enaminoketone derivatives with the sequence of orthogonal phases (CryE)-CryB-HexB-SmA doped by paramagnetic probe revealed angular limitation in the rotation of molecules around their long axes in both CryE and CryB phases, while in the HexB phase limited (series FLU, REF, PIR) and not-limited (series RFL) rotation was observed. Moreover, two types of the restriction degree versus temperature were found. In FLU the limited rotation seems to be induced by the precedent CryB phase, while for REF compounds is inherent property of the HexB phase. The limited rotation is very likely attributed to molecular herring bone order (HBO), wide-spread of which in Hex B phase is still under question. So, this work is the first attempt not only to suggest a simple way to establish HBO, but to get its quantitative description. Previous investigation [1] of PIR and RFL compounds provide the non-XY critical exponent  $\beta$  for HexB - SmA phase transition. Thus it might suggest that non-XY behaviour of HexB phase is not related to the appearance of HBO. The temperature dependences of order parameters  $\overline{P}_2$ ,  $\overline{P}_4$  and rotational rates around short ( $\tau_0$ ) and long ( $\tau_2$ ) molecular axes in SmA were obtained as well.

[1] E. Gorecka et al, Phys. Rev. E50, 2863 (1994); Europhys Letter 27, 507 (1994).

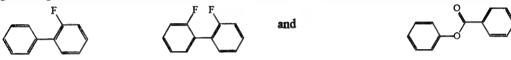
<sup>\*</sup> Supported by ISF Grant MKL 300.

#### THE STRUCTURE OF MESOGENIC FRAGMENTS FROM NMR EXPERIMENT

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The NMR spectrum of liquid crystalline samples can be analysed to give dipolar couplings,  $D_{ij}$ , and quadrupolar,  $\Delta v_i$ , splittings. These are averages over motion of the whole molecule and of internal bond rotations. The data may be interpreted with the aid of mean field models to determine the conformational distribution, and the orientational order, and how these are inter-related. Examples will be discussed of the application of this technique to studying the mesogenic fragments



[1] Liquid Crystalline Samples: Structure of Nonrigid Molecules. J.W.Emsley.

The Encyclopedia of NMR, eds. D.M. Grant and R.K. Harris, John Wiley and Sons Chichester 1996.

**B3P.27** 

TEMPERATURE DEPENDENCE OF ATOMIC DISPLACEMENT PARAMETERS AND ORDER PARAMETERS IN THE CRYSTALLINE PHASE OF A MAGNETIC COMPOUND, S.K.Giri\*, P.K.Mandal, S.Paul and R.Paul, Department of Physics, North Bengal University, Siliguri, Darjeeling, Pin-734430, W.B., India.

Rigid body model has been applied for vibrational analysis of the molecule 5-(trans-4-Heptylcyclohexyl) -2-(4-Cyanophenyl) Pyrimidine. The crystal structures of this compound have been determined at 300°K and 243°K. The anisotropic thermal parameters have been analysed at these temperatures in terms of assumed overall rigid body motion for the whole molecule and for molecular fragments. The mean squares(M.S) amplitudes of librational motion have the largest values about the molecular long axes. M.S amplitudes of translational motions have smallest values along the stacking directions and largest values along the molecular long axes. At low temperature these values are much smaller than those at room temperature. Order parameter in the crystalline phase have been calculated with a correction due to librational motion. Attempts have been made to explain the transition from crystalline phase to mesomorphic phase in the light of these analyses.

\* Junior Research Fellowship sponsored by Department of Atomic Energy, India.

**B3P.28** 

LANGMUIR-BLODGETT TECHIQUE AS A METHOD FOR FORMATION THIN ORDERED LIQUID CRYSTAL FILMS, <u>Valkova L.A.\*</u>, Problem Laboratory of Liquid Crystals, Ivanovo State University, 153048 Ivanovo G. Chlebnikova 36, 189, Russia

The Langmuir-Blodgett (LB) technique for formation thin ordered films both in crystal and in liquid crystal states was used. For some compounds this is only method for forming ordered samples. Langmuir-Blodgett films of series of tetraalcanoiloxigidrochinons, copper carboxylates, hexaalkoxitriphenilens and crown ethers were formed. Compounds of these series form discotic or nematic liquid crystal phases. The stucture of LB films both in solid and in liquid crystal states were investigated by the X-Ray diffraction and electron diffraction methods.

\*Supported by Russian FFI Crant 96-02-19036 and international programm "OMMEL"



# OPTICAL BIAXIALITY OF A FREELY SUSPENDED FILM IN THE SMECTIC A PHASE

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In our group the influence of angles in the mesogenic core on the liquid crystalline behavior and on the rotation around the mesogen long axis is studied. A strong bias in the rotation should lead to a board like shape of the mesogenic unit revealing biaxial properties in the nematic and in the smectic A (S<sub>CM</sub>) phase. We present the results of conoscopic investigations on an Oxadiazole derivative with the phase behavior: K 220 S<sub>C</sub> 235 S<sub>A</sub> 295 I [°C]. Owing to the high transition temperatures of the investigated liquid crystal, coatings of the glass plates for sample alignment were not accessible. In order to obtain homeotropic alignment for the conoscopic experiment, freely suspended films were prepared. After applying an electric field on the sample in the smectic C phase and slow heating to the smectic A phase the biaxial interference patterns indicating the existence of the S<sub>CM</sub> phase can be observed.

#### **B3P.30**

MESOGENIC HOMOPOLYMERS OF 4-HYDROXYCINNAMIC ACID, <u>D.N.</u>
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of Technology and Engineering, Post Box No 51. M.S. University
of Baroda, BARODA - 390 001, INDIA.

4-Hydoxycinnamic acid is homopolymerized by using different solvents and thionyl chloride as condensing agent. Heating in a non-polar solvent at lower temperatures gives 'oligomers' which exhibit mesomorphism. When a tertiary base [1] is used as catalyst, high molecular weight polymers are obtained which are non-mesogenic. Polymers are characterized by elemental analysis, spectroscopic analysis and viscometry.

[1] H.G. Elias, J.H. Tsao, and J.A. Palacious, Macromol. Chem. 186, 893 (1985).

# **B3P.31**

IONIC LIQUID CRYSTALS AND GLASSES IN ALKANOATE SYSTEMS, T.A.Mirnaya\*, Institute of General and Inorganic Chemistry, Kiev, 252680 Ukraine, and P.Ferloni, Università Degli Studi di Pavia, Dipartimento di Chimica Fisica, Pavia, 27100 Italy

More 40 phase diagrams of binary systems of metal alkanoates with short length of alkanoate chain  $C_nH_{2n+1}COO^-$  ( $n_c=1-5$ ) are studied and classified. The thermotropic and lyotropic nature of ionic mesophase formation is considered. The effect of metal cation and organic anion parameters on the ionic mesophase formation are described and discussed relative to electrostatic stabilization of liquid crystalline ordering. The conditions to yield the glassy ionic smectics at ambient temperatures are established. The specific properties of ionic smectic glasses such as the surface conductivity, the capability to be both orienter and polarizer simultaneously, et al. are reported.

<sup>\*</sup>Supported by INTAS Grant 93-2649.

# LOCAL FIELD AND ORDER PARAMETER OF 4-ALKYL-4'-ALKOXY-TOLANES,

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The parameters of microscopic structure of twelve 4-alkyl-4'alkoxytolane substances such as local field anisotropy df/<f>, Lorentz tensor L , order parameter S were calculated on the base of refractometric measurements. We have used Averyanov's suggestion of proportionality of temperature dependences of anisotropy tensor t = 1/3 - L and birefringence. The order parameter was calculated in approaches of zero and anisotropic local field. The formfactor of elementary cavity in calculations of Lorentz tensor was equal to the shape of a space which a molecule occupies (shape of excluded volume) [1]. For substances investigated (the shortest - 4-pentyl-4'-methoxytolane and 4-butyl-4'-ethoxytolane, the longest one - 4-heptyl-4'-pentoxytolane), the values of L vary from 0.396 to 0.384, df/<f> from -0.03 to -0.09, S at Tni - T =10 K from 0.69 to 0.56 for the case of anisotropic local field or from 0.63 to 0.51 for df=0, ne from 1.74 to 1.65, no from 1.53 to 1.49, birefringence from 0.21 to 0.15. We dicuss the dependence of physical parameters values on substituents conformations from the point of view of different molecular models.

[1] V. Belyaev, MCLC 265, 675 (1995).

**B3P.33** 

POLYMOPHISM AND STRUCTURE 4-CYANO-4'-PENTALKOXYBIPHENIL AN MESOMOR-PHIC STATE, L.M.Babkov, O.V.Gorshkova, G.A.Puchkovskaya<sup>1</sup>, I.N.Khakimov<sup>2</sup>, Saratov State University, 410071, Saratov, Russia; <sup>1</sup> Institute of Physics, National Academy of Sciences of Ukraine, 252028, Kiev, Ukraine; <sup>2</sup> Samarkand State University, 703000, Samarcand, Uzbekistan.

Polymorphism and mesomorphic state of 4-cyano-4'-pentalkoxybiphenyl (5OCB) has been investigated by IR spectroscopy (experiment, theory) method. The specimens has been investigated over a temperature range 100-500 K. The spectra has been recorded in the range 33-4000 cm<sup>-1</sup>. The temperature induced changes of the IR spectra has been described on the basis of a working hypothesis on conformational mobility of 5OCB molecule and theoretical modelling of its spectra. Both changes in the conformational composition at increasing temperature and the presence of several conformers realized simultaneously in the same specimens over certain temperature intervals has been detected. The conformations of 5OCB molecule with planar biphenil fragment realized in all phase states. The angle besides biphenil fragment and alcyl radical decrease from 35 grade in solid crystal phase to 10 grade in liquid crystal phase and isotropic liquid.

**B3P.34** 

SPONTANEOUS AND INDUCED CHIRALITY OF NEMATIC LIQUID CRYSTALS, Serguey Shiyanovskii and Julie Terentieva, Institute for Nuclear Research, 252028, Kiev-28, Ukraine

The theory of spontaneous and induced deracemization of nematogenic molecules with a low energy barrier between enantiomers is developed for nematic (N) and cholesteric (C) phases. The spontaneous deracemization may be caused by different anisotropic interaction between enantiomers [1]. The correlation between spontaneous deracemization and orientational order results in the appearance of new phase diagrams I-N-C and I-C with the first order phase transitions (I - racemic isotropic phase). If the transition time between enantiomers are large, the lifetimes of metastable phases strongly increase leading to the temperature hysteresis and monotropism of the nematic phase. It is shown that the deracemization induced by interaction with chiral dopants in nematic-cholesteric mixtures can be the origin of two cholesteric phases  $C_1$  and  $C_2$  with the first order phase transition between them.

1. Ju.G.Terentieva, S.V.Shiyanovskii, Sov. Phys. JETP 75, 645 (1992).

DEUTERIUM NMR STUDIES ON LIQUID CRYSTALLINE MOLECULES WITH SELECTIVELY DEUTERATED CYCLOHEXANE RINGS, <u>Junko Sano</u>, Haruyoshi Takatsu, Sadao Takehara, and Hirokazu Toriumi\*, Dainippon Ink & Chemicals, Inc., 631 Sakado, Sakura-shi, Chiba 285, Japan; \*Department of Chemistry, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan.

Deuterium NMR spectroscopy has emerged as a powerful technique to elucidate the conformational and orientational properties of liquid crystalline molecules. This paper reports the results of <sup>2</sup>H-NMR analysis of a new class of liquid crystals with selectively deuterated cyclohexane rings. The observed <sup>2</sup>H-NMR spectrum in a nematic phase consists of a superposition of discrete quadrupolar doublets associated with the axial and equatorial deuterons. The quadrupolar coupling constants determined for orientationally inequivalent deuterons are then used to evaluate the orientational order parameters of the cyclohexane ring. Temperature dependence of the orientational order parameter, its biaxiality, and the alignment angle of the molecular principal axis will be discussed by combining the <sup>2</sup>H-NMR observations with the results of molecular orbital calculations.

### **B3P.37**

<sup>14</sup>N NUCLEAR QUADRUPOLE DIPS IN THE PROTON SPIN--LATTICE RELAXATION DISPERSION IN THE SMECTIC PHASE OF HpAB, Esteban Anoardo and Daniel J. Pusiol, FAMAF, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, ARGENTINA<sup>(\*)</sup>.

We have carefully measured the proton spin-lattice relaxation dispersion in the Larmor frequency region of the previously reported proton-nitrogen level crossing produced quadrupole dips [1]. The stability and precision of the low relaxation Zeeman field of our Fast Field Cycling NMR spectrometer were tested by irradiating the protons of a sample of water with a second radio frequency.

Four chemically nonequivalent Nitrogen nuclei were detected, implying that the smectic C\* phase is locally composed by bimolecular unit cells.

[1] D. Pusiol and F. Noack, Liq. Cryst., 5, 377 (1989).

(\*) Work granted by CONICET, CONICOR and Fundación Antorchas of Argentina.

#### **B3P.38**

NQR LINESHAPES IN LIQUID CRYSTALLINE MESOPHASES, Daniel Pusiol, Cecilia González y Esteban Anoardo, FAMAF, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, ARGENTINA.

Nuclear Quadrupole Resonance lineshape of the <sup>14</sup>N in smectic HpAB and of the <sup>35</sup>Cl in 4-chlorophenyl-undecyloxybenzoate has been measured by the cross relaxation quadrupole dips in the proton spin-lattice relaxation and by a zero-field double nuclear quadrupole resonance experiment.

The measured lineshapes and local molecular ordering are related by means of a Montecarlo simulation of the mycroscopic molecular arrangement.

(\*) Work granted by CONICET, CONICOR and Fundación Antorchas of Argentina.

LOW VOLTAGE VERY FAST ELECTROCLINIC MATERIALS. NEW MOLECULAR APPROACH, L.A.Beresnev, A.Biradar\*, W.Dultz#, S.A.Pikin§, and W.Haase, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, 64287 Darmstadt, Germany,\*National Physical Laboratory, New Delhi, India, #Deutsche Telekom AG, Am Kavalleriesand 3, 64276 Darmstadt, Germany, §Institute of Crystallography Russ.Acad.Sci., Leninskii prosp.59, 117333 Moscow Russia.

We propose the detailed approach for practical creation of electroclinic materials, based on microscopic consideration of molecular structures of basic constituents parts of mixtures, prepared from smectic A matrix and chiral impurities, inducing the electroclinic properties. According to our approach the mixture, containing a relatively small concentration of chiral dopants in smectic matrix, will have the switching and dielectric properties, which can be described as a molecular process rather than collective (like soft or Goldstone) modes. Taking into account the mutual lengths and tilt angles of molecular cores of both subsystems, the materials with response time of order of hundreds of nanoseconds at room temperature and small driving voltages can be made. We present the experimental data on especially designed mixtures, showing the much more complicated behaviour of tilt angle, spontaneous polarization, switching time, rotational viscosities and dielectric relaxation parameters, as it is commonly considered with phenomenological models. The applicability of proposed approach is confirmed with the high performance of developed electroclinic materials.

INDUCED SMECTIC AND CHIRAL SMECTIC PHASE IN RACEMIC MIXTURE OF CHOLESTERYL COMPOUND

**B3P.40** 

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racemic mixture of cholesteryl chloride and cholestervl critical myristate exhibit a compensated nematic phase at concentration and temperature. 72.3% of cholesteryl 56°c. The exhibit compensated nematic phase at the temperature concentrations from 10 to 90% of cholesteryl chloride exhibit cooled induced smectic A phase when the specimen from isotropic phase. Induced smectic A phase and chiral mixtures of with 30 to 75% are obtained in the at intermediate temperature. Typically the cholesteryl chloride mixture with 72.3% cholesteryl chloride exhibit I-Sa-Se\*-Sa-C phases sequentially. X-ray diffrction, DSC and optical texture studies have been carried out for five concentrations. The pitch and tilt angle of the chiral smectic phase measured. Interesting optical textures are also illustrated.

 H.Stegemeyer, R.Meister, H.J.Altenbach and D.Szewczyk, Liq.Cryst; 14, 1007 (1993).

**B3P.41** 

PHYSICAL PROPERTIES AND APPLICATION OF LIQUID CRYSTALS HAVING A DEUTERATED CYCLOHEXANE RING, <u>H.Ohnishi\*</u>, K.Takeuchi, N.Ishida, S.Takehara, M.Osawa, S.Ogawa, S.Shirokura\*, and H.Takatsu, Lodic Co., Ltd\* and Dainippon Ink Co.,Ltd., 4472-1, Komuro, Inamachi, Kitaadachi-gun, Saitama, 362

Transition temperatures, enthalpies, elastic constants and dielectric anisotropies of newly developed liquid crystals with deuteriated cyclohexane rings are measured and compared with those of the corresponding non-deuteriated liquid crystals. The deuteriation of cyclohexane ring reduces the melting point and the melting enthalpy. The elastic constants and elastic constant ratio  $K_{33}/K_{11}$  are also discussed. The liquid crystal mixtures of low melting point and high clearing point with keeping high voltage holding ratio and quick response are developed and their performance for AM-LCD is discussed.

TWO CRYSTALLINE BEHAVIOUR BINARY MIXTURES LIQUID NONMESOGENIC COMPOUNDS. and LokanathaRai.K.M. Nagappa, Hanumantha Naik.R, Mahadeva.J Alapati.P.R\*; of Mysore. Department of Physics, University Studies in Manasagangotri, Mysore - 570 006. \*Department of Chemistry, University of Southampton, SO17,IBJ,UK. Department of Chemistry, University of Mysore, Mysore-6.

Binary mixtures of two novel amphiphilic mixtures of tetradecanol (TDC) and orthophosphoric acid ( $H_{\rm S}PO_{4}$ ) exhibit an interesting liquid crystalline phases in large range of concentration and temperature. The mixtures in the concentration range between 10 to 25% of TDC shows smectic A and cholesteric phases at higher The mixtures respectively. temperatures and room concentration 26 to 50% of TDC in H<sub>2</sub>PO<sub>4</sub> exhibit smectic A, smectic C and smectic E phases. The mixtures with higher concentration of H<sub>2</sub>PO<sub>4</sub> exhibit nematic and smectic phases. The temperature dependence of orientational order parameter nematic phase and molecular order in nematiods drops are also discussed. X-ray, DSC, Optical, IR and NMR studies have been carried out. Optical microscopy suggest that the mesophase with higher concentration of TDC at higher temperature is a discotic hexagonal phase.

1) N.Boden and M.C.Holms, Che Phys letter 105, 176, 1984.

**B3P.43** 

ESTIMATING DIELECTRIC ANISOTROPY OF LIQUID CRYSTAL COMPOUNDS, G. Saitoh, M. Satoh, E. Hasegawa, Functional Devices Res. Labs., NEC Corporation, Kanagawa, 216, Japan

We have developed an improved method of determining dielectric anisotropy ( $\Delta\epsilon$ ) for liquid crystal compounds by using molecular orbital (MO) calculations and the Maeir-Meier equation[1]. The method involves calculation of the dipole moment ( $\mu$ ) and the anisotropy of polarizability ( $\Delta\alpha$ ) with the MO method, and substitution of these parameters into the Maeir-Meier equation. These calculations are repeated until the calculated  $\Delta\epsilon$  saturates. As the results, the estimated  $\Delta\epsilon$  agree closely with those obtained experimentally for liquid crystal compounds with various skeletons and polarized groups (for example, experimental data: 18.0 calculated  $\Delta\epsilon$ : 14.6 on 4-pentyl-1-(4-cyanophenyl)cyclohexane (PCH5), and correlation coefficient: R=0.99). Since  $\Delta\epsilon$  is the main factor affecting the threshold voltage, the developed method is useful for molecular design of liquid crystal compounds with controlled properties.

[1] W. Maier and G. Meier, Z. Naturforsch., 16a, 262 (1961)

**B3P.44** 

THE PAIR INTERMOLECULAR INTERACTION ENERGY FOR THREE MESOGENIC CRYSTALS, P.K. Sarkar, S. Paul and P. Mandal, Physics Department, North Bengal University, Darjeeling-734430, INDIA.

An atom-atom potential is used to determine the minimum energy configuration for a pair of molecules of the ethyl, pentyl and heptyl members of the homologous series 5-(trans-4-alkylcyclohexyl)-2-(4-cyanophenyl) pyrimidine. The first two compounds have nematic phase, the third one has smectic phase as well. The geometry of the molecules were based on the crystal structure data [1]. A Buckingham type potential has been used for Van der Waals interaction. Electrostatic contribution to the potential energy were also calculated, partial atomic charges were determined using MNDO method. Computations have been carried out by keeping one molecule fixed, moving the other molecule along three axes and rotating around them with a resolution of .1 Å for translation and 1° for rotation, molecules were assumed rigid. Both parallel and anti-parallel combinations of molecules were considered. Stacking, in-plane and terminal interaction energies were calculated. Van der Waals interaction plays predominant role in dimer stabilization. The compounds minimize for nearly the same energy value for the parallel and anti-parallel combinations. Results have been discussed in view of experimental evidences.

[1] P.Mandal, B.Majumdar, S.Paul, H.Schenk and K.Goubitz, Mol. Cryst. Liq. Cryst., 168, 135(1989); Mol. Cryst. Liq. Cryst., 180B, 369(1990); Mol. Cryst. Liq. Cryst., 195, 149(1991).

FAST STOCHASTIC REORIENTATIONS IN NEMATIC AND ISOTROPIC PAA AND PAP R.Podsiadły<sup>#</sup>, J.Mayer, J.A.Janik, J.Krawczyk, # - Faculty of Chemistry of the Jagiellonian University, 30-060 Kraków, Poland. - H.Niewodniczański Institute of Nuclear Physics, 31-342 Kraków, Poland.

The incoherent quasi-elastic neutron scattering (QNS) measurements with a narrower (HWHM=30µeV) energy resolution than in paper [1] were carried out for PAA and PAP in both nematic and isotropic phases. Fitting procedures done for various models of stochastic motions showed that it is necessary to take into account the reorientational motion of the whole molecule around its long axis, besides the reorientations of molecular fragments introduced in [1]. The time scale of motions of whole molecules is in good agreement with relaxation times obtained previously in the dielectric measurements.

[1] R.Podsiadły, J.A.Janik, Mol.Cryst.Liq.Cryst. 262, 285 (1995)

**B3P.46** 

# EFFECT OF CHAIN LENGTH ON ORIENTATIONAL RELAXATIONS IN SMECITIC POLYMORPHISM

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Systematic low frequency dielectric investigations are carried out in the 100.m homologues (m = 8, 9 & 10) of schiff base liquid crystalline no.m compounds, viz., N(p-n-alkoxybenzilidene)p-n-alkylanilines. Cole-Davidson resolved dielectric spectra infer [1] multiple relaxations of type 1 and type II in smectic-A and smectic-C phases. Higher frequency relaxation associated with type 1 relevant to the dipolar reorientation of central rigid core is found to decrease with the increasing alkyl end chain length from 8 to 10. The Smectic-A and Smectic-C dielectric spectrum analysed in the wake of the reported [1] Arrhenius temperature dependence of relevant smectic phase relaxations along with the unified smectic temperature T<sup>U</sup> infers the disordering effect of increasing chain length.

[1]. G.P.Rani, D.M.Potukuchi, N.V.S.Rao and V.G.K.M.Pisipati, Solid State Commn., 92, 349 (1994).

**B3P.47** 

KINETIC FEATURES OF RADICAL REACTIONS IN THERMOTROPIC LIQUID CRYSTALS. T.I.Shabatina, V.A.Batyuk, <u>G.B.Sergeev\*</u>, Dept.of Chemistry, Moscow State University, Moscow 119899, Russia.

The brief review on the kinetics of some thermo- and photoinduced free radical reactions in nematic, cholesteric, smectic and reentrant nematic phases is presented. The effects of reagent molecules ordering are considered on the following examples: primary radicals escape and free radicals 'cage' recombination during photo and thermo degradation of radical precursors, competitive interaction of primary radicals with acceptors of different molecular structures, interaction of alkyl radicals with nonsaturated organics in nematic phase, photoinduced nitroxide radical formation in different low temperature states of alkyl(alkoxy)cyanobiphenyls. The role of entropy and energetic factors in radical reaction kinetics in liquid crystalline media is analysed. The kinetic model described the reaction rate dependence on order parameter of nematic system is proposed.

\*Supported by National Federal Programme "Russian Universities"

DIMERIZATION OF SOME LIQUID CRYSTALLINE ALKYLCYANOPHENYLS IN BULK AND INERT MATRICES. <u>T.I.Shabatina</u>, E.V.Vovk, T.V.Khasanova, Yu.N.Morosov, G.B.Sergeev\*, Dept. of Chemistry, Moscow State University, Moscow 119899, Russia

Molecular association of liquid crystalline 4,4'-pentylcyanobiphenyl(5CB), 1-p-cyanophenyl-4-pentylcyclohexane (5CH), 2-p-cyanophenyl-5-pentylpiridine (5Py) has been studied in bulk, solutions and inert matrices at 77-330 K by low temperature reflection IR-spectroscopy and isothermal Calve calorimetric method. IR-study of thermal behaviour of molecular cyanobiphenyl films obtained by condensation of molecular beam on cooled copper surface showed the effective inner dimers formation at 270-290 K. This transformation was accompanied by CN-stretching band to lower frequencies. This blue shift due to dimerization process was confirmed by of computer modelling of theoretical spectra. More precise data were obtained by isolation of monomer and dimer species in low temperature matrices of Ar at 5-10 K and hydrocarbon at 77-100 K. The computer treatment of experimental data for bulk liquid crystals at different temperatures allowed us to obtain the values of association enthalpy 19 (5CB), 12 (5Py), 3(5CH) kJ/mol. It was found that characteristic time of molecular association in mesophase is about 300 s, that is significantly more than specific time of diffusion processes.

\*Supported by National Federal Programme "Russian Universities "

# **B3P.49**

TILTED AND ORTHOGONAL SMECTICS IN THIENYL AND FURYL SUBSTITUTED ENAMINOKETONES, J.Szydlowska, D.Pociecha, A.Krowczynski, E.Gorecka Department of Chemistry, Warsaw University, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland.

The influence of the molecular bending on the appearance of the tilted liquid crystalline phases was examined for thienyl and furyl substituted enaminoketones. In the homologous series with 2-buthylthienyl and 2-hexylthienyl moieties (TH4 and TH6 respectively) terminated by the alkoxy chains only the tilted smectics were found. For the compounds with the non-substituted thienyl ring (TH0) merely orthogonal phases were established while for 2-methylthienyl series (THI) [1] the mixed type phases were observed. The above results shows that increasing molecular bend promotes the tilted liquid crystalline phases. For the more bent compounds, containing in the mesogenic core the furyl ring even the non-substituted derivatives (FU0) reveals both tilted and orthogonal smectics that confirms strong relation between the molecular shape and the smectic properties.

In all compounds of TH0 series the appearance of the transition bars at SmA-HexB phase transition, that are usual for the strongly first order SmA-CryB transition, seems to be related to the sufficiently narrow (about 4°C) and constant temperature range of the HexB phase and suggests the discontinuity of the hexatic structure development.

[1] W.Pyżuk at al, Phys.Rev.E. 52, (1995).

#### **B3P.50**

A STUDY OF THE ORDER PARAMETERS OF FOUR SERIES OF LIQUID CRYSTALS BY ONE AND TWO DIMENSIONAL <sup>13</sup>C NMR, <u>T.-H. Tong</u> and B. M. Fung, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019-0370, U. S. A.

The orientational ordering of twelve liquid crystals in four series of homologous compounds, namely 4-n-alkoxybenzilidene-4'-n-alkylaniline (nO.m), 4-n-alkylphenyl-4'-n-alkoxyphenylbenzoate (nOm), 4-n-alkoxyphenyl 4'-n-alkoxyphenylbenzoate (nOm) and 4, 4'-di-n-alkyldiphenyldiacetylene (PTTP), has been studied at different temperatures by 2D  $^{13}$ C NMR with variable angle sample spinning. The carbon-proton dipolar coupling constants were obtained and the order parameters of the aromatic cores were calculated. The  $^{13}$ C chemical shifts for each carbon nucleus in the aromatic cores were measured against temperature. A linear dependence between the chemical shifts and the order parameters was observed within each homologous series. The results furnish a useful and convenient database for the evaluation of order parameters for these four series of liquid crystals from simple measurements of  $^{13}$ C chemical shifts.

PRODUCING AND SPECTROSCOPIC STUDY OF LOW TEMPERATURE SILVER COMPLEXES WITH MESOGENIC CYANOBIPHENYL DERIVATIVES, T.I.Shabatina, <u>E.V.Vovk</u>, A.V.Vlasov, G.B.Sergeev\*, Department of Chemistry, Moscow State University, 119899 Moscow, Russia.

Metal containing liquid crystalline systems were obtained by co-condensation of metallic silver vapour with evaporated liquid crystalline 4-pentyl-4'-cyanobiphenyl (5CB) under conditions of molecular beams. The film samples for IR-study were obtained by deposition on cooled by liquid nitrogen polish copper surface using specially constructed vacuum cryostat. The residual pressure in the system was not more than  $10^{-4}$  Torr. The registration of IR-spectra was carried out using reflection mode. Comprehensive IR-study of Ag-5CB film samples of different component ratio at 80K shows the existence of Ag-5CB complexes due to Ag interaction with  $\pi$ -electrons of CN bond of cyanobiphenyl molecules. It was indicated by the appearance of two new bands in the region of CN bond vibration at 2080 and 2130 cm<sup>-1</sup>. We considered these bands as CN stretching vibrations in Ag-5CB  $\pi$ -complexes of two types that differed by metal-ligand ratio. The shift of about  $100 \text{ cm}^{-1}$  to lower frequencies is similar to formation of  $\pi$ -complexes of nonvalent transition metal with  $\pi$ -donating ligands. We also determined the appearance of new band at 650 cm<sup>-1</sup> and assigned it to metal ligand vibrations. These changes disappeared by heating up to the room temperatures. So the Ag-5CB complexes are stable only at low temperatures 80-150 K and decompose by samples heating. "Supported by INTAS Grant 94-4299.

**B3P.52** 

AN INTERESTING INFLUENCE OF MOLECULAR STRUCTURE ON LIQUID CRYSTAL PROPERTIES, Xin-Hua Chen\*, <u>D. M.Walba</u>\*, Renfan Shao<sup>#</sup>, N. A. Clark<sup>#</sup>, \*Dept. of Chem. and Biochem., #Dept. of Physics, University of Colorado, Boulder, CO 80309, USA

It is known that introduction of a nitro group onto a phenyl ring ortho to an alkoxy tail branched at C1 (such as for W314, shown below) gives rise to large Ps. This is due to the large dipole of the nitro group combined with good polar order resulting from steric coupling between the nitro group and chiral center, and is well explained by the Boulder model. However, for FLC applications nitro-substituted materials have some drawbacks. They usually have high viscosity, leading to long response times, and some absorption in the visible, which may be responsible for poor chemical stability in SSFLC cells. During our research on new FLCs for NLO we found that simple modification of the W314 structure can overcome these drawbacks. The LC phase behaviour and other properties of these new materials, indicated below, will be reported.

**B3P.53** 

PREDICTION OF THE TWISTING POWER OF CHIRAL SOLUTES IN LIQUID CRYSTAL PHASES, A. Ferrarini, G. Gottarelli, <u>P.L. Nordio</u>\*, F. Pacchiele e V.P. Shibaev, Dept. of Physical Chemistry, University of Padova, 2 via Loredan, 35131 Padova, Italy

Recently, an expression relating the twisting power of chiral solutes with their shape, in addition to ordering and elastic properties of the solvent, has been derived. Experimental values of the twisting power are compared with those predicted by the model for three groups of chiral molecules, namely heptalene derivatives, molecules with hexahelicene-like structures, and a series of derivatives of binaphthyl in open and bridged forms. The behaviour of the molecules is discussed in terms of a surface tensor, describing how the solutes tend to orient in an anisotropic environment, and an helicity tensor, which gives the molecular helicities as as viewed along different axes. Temperature dependence of ordering matrix and twisting power is interpreted on the basis of the theoretical predictions.

A. Ferrarini, G.J. Moro and P.L. Nordio, Phys. Rev. E 53, 681 (1996); Molec. Phys., in the press. \* PECO Project N. 940602



MAPPING THE CONFORMATIONAL SPACE OF BORON CLUSTER MESOGENS: EXPERIMENTAL AND THEORETICAL MOLECULAR STUDIES, J. Laska, M. K. Patel, and P. Kaszynski. Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN, 37235, USA.

There is little known about the conformational space of 10- and 12-vertex boron *closo*-cluster derivatives. The shape of such a space, defined by steric and electronic interactions, yields information about the density of low energy conformers with extended molecular shape. This, in turn, is an important factor in the design of liquid crystalline materials. The  $C_4$  and  $C_5$  rotational symmetry of the clusters also permit the design of materials with negligible rotational barriers (>1 cal/mol).

Here we attempt to correlate thermal stability of mesophases with the conformational space of 10- and 12-vertex boron cluster derivatives. We also provide X-ray molecular structures of several mesogens.

**B3P.55** 

THE INFLUENCE OF THE MOLECULAR ARCHITECTURE OF POLYPHILIC COMPOUNDS ON THE STRUCTURE OF SMECTIC PHASES, S. Diele, D. Lose, G. Pelzl, F. Guittard\*, E. Dietzmann\*\*, W. Weissflog\*\*, Institut für Physikalische Chemie, Martin-Luther-Universität, D-06108 Halle/S., Germany, \*Laboratoire de Chimie Organique du Fluor, Université de Nice, France, \*\*Max-Planck-Arbeitsgruppe, "Flüssigkristalline Systeme", D-06108 Halle/S., Germany

The structure of smectic phases of selected polyphilic compounds were investigated by X-ray diffraction measurements. The substances studied are (I) rod-like compounds consisting of a biphenyl core one-sided linked with a perfluorinated chain and tricatenar compounds with perfluorinated chains either (II) in the branched part or (III) in the non-branched part of the molecule. The compounds I exhibit a layer structure of  $S_{Ad}$  type which consists of sublayers formed by the aromatic parts and the disordered fluorinated chains, respectively. It is remarkable that the **disordered sublayer** is maintained if the  $S_{Ad}$  phase is transformed into the high-ordered B and E phases. In the substance classes II and III monolayer  $S_A$  and  $S_C$  phases result for packing reasons. Shifting the balance between perfluorinated and aromatic/aliphatic moieties the smectic monolayers are distorted indicated by an out-off axes diffuse scattering at the pattern of well-oriented monodomains. Lowering the temperature the frustration is enhanced so that the layer structure becomes instable and a lamello-columnar phase appears which can be described by a 2 D rectangular centred cell.

**B3P.56** 

STRUCTURE-PROPERTY-RELATIONSHIPS OF LIQUID CRYSTALS BASED ON THE EVALUATION OF THE DATABASE LIQCRYST, <u>V. Vill</u>, Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King Platz 6, D-20146 Hamburg, Germany

The database LiqCryst [1] contains chemical structures and physical properties of more than 65,000 compounds. The aim of the database is not only in the collection of data, but also in the statistical analysis and the prediction of data as well. This program uses the "LEGO"-model of liquid crystals. The chemical structure is subdivided into a linear sequence of fragments. These fragments are rings, bridges, terminal groups etc. Two different chemical substructures can be compared by their transition temperatures, e.g. 1,3-dioxane compounds can be compared with the analogous cyclohexane compounds. A similarity between two chemical structures can be defined by one single difference in the code of fragments. The properties of a new structure can be predicted by the extrapolation from known similar compounds.

[1] LiqCryst, Database of Liquid Crystals, V. Vill, Fujitsu FQS, Fukuoka, 1995; LCI Publisher, Hamburg, 1995.

NON-CONVENTIONAL MESOGENS AND LOW TEMPERATURE SMECTICS PRODUCED BY HYDROGEN BONDS, H. Kresse\*, H. Bernhardt, A. Treybig, W. Weissflog<sup>0</sup>, \*Institut für Physikalische Chemie, Martin-Luther-Universität Halle and Max-Planck-Gruppe, Mühlpforte 1, 06108 Halle, Germany.

A three-fold self-organization process can be observed by mixing of substituted acids as proton donator D and pyridines as acceptor A: the reorganization of new hydrogen bonded associates  $A_xD_y$ , the formation of mesophases and, in the case of chiral components, a helical sub-structure of some phases [1]. Recently it was demonstrated by us that the relative stability of such mesophases shows a maximum at a fixed acidity of A [2]. This experiment was the key to design associates with N,  $S_A$ ,  $S_C$ ,  $S_C^*$ ,  $S_B$ , and at the first time also with  $S_E$  and columnar phases. On the other hand mesogens with an unconventional molecular shape like swallow-tailed and laterally branched molecules can be rebuild from fragments by self-organization. The existence of different associates and phases was proven by spectroscopic, microscopic, calorimetric, electrooptic and X-ray investigations.

[1] T. Kato, H. Kihara, T. Uryu, S. Ujiie, K. Iimura, J. M. J. Frechet, U. Kumar, Ferroelectrics 148 161 (1993). [2] H. Bernhardt, W. Weissflog, H. Kresse, Angew. Chem., appears April 1996.

\* supported by the Deutsche Forschungsgemeinschaft.

**B3P.58** 

INFRARED SPECTROSCOPY OF MOLECULAR ORDER IN DISCOTIC LIQUID CRYSTALS. T.S. Perova<sup>1</sup> and J.K. Vij<sup>2</sup>. <sup>1</sup> Vavilov State Optical Institute, St.-Petersburg, 199034, RUSSIA. <sup>2</sup> Department of Electronic & Electrical Engineering, Trinity College, Dublin-2, IRELAND.

We present investigations of changes of the order parameter and of the frequency maximum of some characteristic bands of discotic liquid crystals with temperature. For these investigations discotic liquid crystals were chosen with different lengths and different types (esters and ethers) of tail and core. These are a triphenylene derivatives: hexa-n-pentyloxytriphenylene (H5T), hexa-n-heptyloxytriphenylene (H7T) and hexa-n-decanoyloxytriphenylene (H0T), truxene and dibenzopyrene. A large value of the order parameter found from IR measurements for H5T and H7T let us to conclude that the cores of these discotic materials are almost perfectly aligned. These results are in good agreement with NMR spectroscopy previously made. However for the material, H0T, our spectroscopic results show a quite small value of the order parameter. The comparison of IR results for discotic liquid crystals with different cores are also discussed.

**B3P.59** 

X-RAY STUDY OF SOME LIQUID CRYSTAL HOMO- AND COPOLYMERS\*, A.I. Alexandrov, T.V. Pashkova and I.I. Konstantinov, Department of Physics, Ivanovo State University, Ivanovo 153025, Russia

We have investigated the stucture of liquid crystal homo- and copolymers based on chiral CH<sub>2</sub>=CH-CH<sub>2</sub>-CH(CH<sub>3</sub>)-(CH<sub>2</sub>)-COO-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-O-C<sub>8</sub>H<sub>17</sub> and achiral CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>6</sub>-O-C<sub>6</sub>H<sub>4</sub>-COO-C<sub>6</sub>H<sub>4</sub>-O-C<sub>6</sub>H<sub>13</sub> monomers and prepared by free radical polymerization. The copolymers had mole content of the chiral component equel to 0.25, 0.50 and 0.75. The chiral homopolymer and the copolymer samples were oriented by magnetic and electric fields in cooling from isotropic phase. The achiral homopolymer was oriented by extending and shearing. X-ray diffraction data obtained in wide temperature range were interpreted with a use of a paracrystal model. All investigated homo- and copolymers have two each tilted smectic phases with bilayer structures but their X-ray patterns show some features of intensity distribution in reflections related to both the orientation manners and the ratio of the chiral and achiral components. Thus 0.25 and 0.75 copolymers oriented in magnetic field have X-ray patterns corresponding shevron and book-shelf structures accordingly. The correlation between the structure of comb-shaped molecules, the bilayer structure and the chirality of smectic phases is considered using a molecular simulation and diffraction calculations from structure models.

<sup>\*</sup>Supported by INTAS Grant 94-1482.

XRAY, DIELECTRIC AND PRESSURE STUDIES ON A COMPOUND EXHIBITING FERRO, FERRI AND ANTIFERROELECTRIC SMECTIC PHASES, S.Chandrasekhar<sup>+</sup>, D.S.Shankar Rao<sup>+</sup>, S.Krishna Prasad<sup>+</sup>, S,Mery<sup>\$</sup> and R.Shashidhar<sup>\$</sup>, <sup>+</sup>Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, INDIA, <sup>\$</sup> CBMSE, Naval Research Laboratory, Washington DC 20375-5348, USA

We report Xray layer spacing, dielectric constant and high pressure measurements on 1-(R)-[1-S(ethoxy carbonyl) ethoxy carbonyl] ethyloxycarbonyl-4'-(9-decenyloxy) biphenyl-4-carboxylate which exhibits the following sequence of phase transitions: Sm A-Sm C\*-Sm  $C_{\gamma}^*$ -Sm  $C_{\gamma}^*$ -hexatic  $I_A^*$ -crystal K. The P-T diagram shows two three-phase meeting points, which are topologically consistent with critical end points, and reentrant behavior of the C\* and  $C_{\gamma}^*$  phases as the pressure is varied at constant temperature. We also show that the dielectric measurements in the presence of a DC bias field can be used to map the temperature-electric field phase diagram. Results on another compound having a similar molecular structure and exhibiting a direct Sm C\*-Sm  $C_A^*$  transition, will also be presented.

**B3P.61** 

NEW 1R,4R-MENTHAN-3-ONE DERIVATIVES AS CHIRAL COMPONENTS OF THE INDUCED CHOLESTERIC SYSTEMS, <u>L.A. Kutulya</u>, V.V. Vashchenko, V. Danilchenko, Institute for Single Crystals, Academy of Sciences of Ukraine, 60 Lenin Ave, Kharkov 310001, Ukraine.

Two series of new non-mesogenic chiral compounds were obtained and their behaviour as chiral dopants (CD) in nematic and SmA LC were investigated. CD I and II exhibit a high twisting power  $\beta$  in nematics, independent of terminal alkyl length:  $|\beta|$  ( $\mu$ m<sup>-1</sup>·mol.fr.<sup>-1</sup>) for I 51.4–54.0(MBBA) and 38.7–43.3 (5CB); for II 45.1–48.5 (MBBA) and 41.3–44.0 (5CB)]. The dopants influence on thermostability of N\* and SmA phases in their mixtures with 8CB are characterized by linear regression slope values of corresponding dependences of phase transition temperatures on CD concentration (parameters  $A_{N^*}$  and  $A_{SmA}$ ). CD destructive influence on LC phases decreases and changes into stabilizing effect when terminal alkyl chain is elongated, or (to a great extent) by enlarging of  $\pi$ -electronic core

anisometry. CD influence is more essential for SmA-N\* transition than for N\*-Iso one (a wider variation range for  $A_{SmA}$  than for  $A_{N*}$ ). The relationships mentioned are shown to have a general character, at least for anisometric chiral compounds. Their interpretation was given.

DETERMINATION OF THE NEMATIC ALIGNMENT AND ANCHORING STRENGTH AT THE CURVED NEMATIC-AIR INTERFACE, M. Slavinec<sup>1</sup>, S. Kralj<sup>1,2</sup>, S. Žumer<sup>2</sup>, G. P. Crawford<sup>3</sup>, Department of Physics, University of Maribor, Koroška 160, 2000 Maribor, Slovenia, Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia, Xerox Paolo Alto Research Center, 3333 Coyote Hill Road, Paolo Alto, California 94304, USA

We developed a method to determine the surface anchoring strength and the tilt of nematic molecules at the curved nematic-air interface. The method is based on the comparison of the interference textures obtained by polarization microscopy experiment to the ones obtained by numerical of a nematic liquid crystal which partially fills a cylindrical tube enforcing homeotropic anchoring. We focused in particular to the tilt  $\theta$  of nematic molecules from the homeotropic direction on the nematic-air curved interface in the tube of radius  $R \ge 100 \, \mu m$ . The director field is obtained via a minimization of the Frank free energy supplemented by the Rapini-Papoular surface term. The comparison of simulated and experimental textures reveals the anchoring strengths  $W_a$  at the nematic-tube and nematic-air interface as well as the tilt  $\theta$  at the nematic-air interface. For the nematic liquid crystal ZLI 2860 we obtain  $\theta = 7^0 \pm 1^0$ ,  $W_a = (1.5 \pm 0.5) \cdot 10^{-6} \, J/m^2$  at the nematic-tube and  $W_a > 10^{-5} J/m^2$  at the nematic-air interface.

**B4P.02** 

#### LIGHT SCATTERING BY THIN NEMATIC LIQUID CRYSTAL FILMS,

S. Stallinga<sup>1</sup>, M.M. Wittebrood<sup>2</sup>, D.H. Luijendijk<sup>2</sup> and Th. Rasing<sup>2</sup>, (1) Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands, (2) Research Institute for Materials, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

The scattering of light by thin nematic liquid crystal films is studied. In contrast to bulk nematics fluctuations with wavevectors not equal to the difference between the wavevectors of the scattered and the incident light ray can contribute to the scattering. The distribution of fluctuation wavevectors relevant to the scattering is peaked around this difference and has a width inversely proportional to the film thickness. Furthermore, only a discrete set of fluctuation wavevectors is allowed due to restrictions imposed by the boundary conditions. It appears that the confinement causes a decrease of the relaxation times of the different fluctuation modes. In the limit of vanishing film thickness the relaxation time goes linearly to zero with the thickness. This dependence seems to agree with experiment. Similar results may be expected for other confined nematic systems, e.g. for nematics confined to porous media.

B4P.03

DETERMINATION OF THE SURFACE ANCHORING POTENTIAL OF OPTICALLY BUFFED SURFACES, T. Kosa, P. Palffy-Muhoray, J. Li, C. Titus, Liquid Crystal Institute, Kent State University, Kent, OH 44242 USA

Using a magnetooptic method, we have determined the anchoring potential as a function of intensity and wavelength for a variety of dye-doped polyimide alignment materials. We measure the transmittance of a cell between crossed polarizers as a function of the applied magnetic field. By comparing the results of experiments with the model calculations, we obtain the azimuthal anchoring potential as a function of director angle. We compare the anchoring potential to that of mechanically buffed surfaces.



THE RELATION BETWEEN THE MICRO-STRUCTURE OF THE RUBBING FIBER AND THE SHAPE OF THE MICROGROOVE OF POLYMER AND ITS ANCHORING STRENGTH, <u>Kazuhiro Wako</u>, Kwan-Young Han, and Tatsuo Uchida, Department of Electronic Engineering, Faculty of Engineering, Tohoku University, Sendai, Miyagi, Japan.

In order to clarify the surface alignment mechanism of liquid crystal in detail, we have tried a symplified rubbing by using only one fiber[1] and observed the microgroove on the rubbed polymer surface. It is considered that the microgroove is formed by the micro-structure of the edge of the rubbing fiber. Then, we compared the curvature of microgroove structure observed by AFM and FFM with that of the fiber observed by SEM. From the result, we confirmed that they agreed well with each other, therefore, we concluded that the structure of microgroove is determined by the micro-structure of the edge of the fiber. Then, we measured the anchoring strength of the polymer surfaces[2] rubbed by three kind of fiber and compared it with the microgroove structure. From the result, we found that the wider the width of microgroove was, the larger the anchoring strength became. This fact suggests us that the anchoring strength becomes larger as the ratio of rubbed area of polymer surface is larger.

[1] Isao Nakamura: Private communication [2] Y.Sato, K.Kato, T.Uchida: Jpn. J. Appl. Phys. vol. 31 (1992) L579.

#### **B4P.05**

STUDIED OF THE THERMAL STABILITY OF THE LIQUID CRYSTALS ALIGNMENT LAYER BY LINEARLY POLARIZED UV-CURED PHOTOPOLYMERS. Zhenjun Ma, Ruipeng Sun, Kai Ma, Tao Yu, Yafang Liang, Hai jing, Xiling Zhu, Ximin Huang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021

Recently nonrubbed alignment of liquid crystals has been of much interest, because it is a method that has many advantages. In this paper, we studied experimentally the thermal stability of alignment layer form by linearly polarized UV-cured photopolymers. With diffirent UV-cured conditions (UV intensity, irradiate time) and the phtopolymers heat treatment processes, we studied the dependence of the surface azimuthal anchoring energy for pure nematic liquid crystals on temperature, the experimental results will be presented in the paper. We also discuss the aligning ability and anchoring intensity of the UV-cured photopolymers.

#### **B4P.06**

LIQUID CRYSTAL ALIGNMENT FILM WITH MIXTURE OF POLYIMIDE AND SIDE CHAIN LC BY LANGMUIR-BLODGETT TECHNIQUE, Young-Mo Koo<sup>1</sup>, Mu-Hyun Kim<sup>1</sup>, MyongSoo Lee<sup>2</sup>, and Jong-Duk Kim<sup>1</sup>, <sup>1</sup>Department of Chemical Engineering, KAIST, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701 Korea. <sup>2</sup>Department of Chemistry, Yonsei University, Seoul, 120-749 Korea.

The mixed film of polyimide and a side-chain liquid crystal, 11-[(4-cyano-4'-biphenyl) oxy] undecanyl vinyl (CN-11-M)[1] ether were investigated as a LC alignment film to increase the pretilt angle of a nematic LC. The mixed film was fabricated by the Langmuir-Blodgett technique. A stable monolayer of poly (amic acid) alkylamine salt(PAAS) and CN-11-M was formed at the air-water interface. A Y-type film on ITO glass was established at 25 mN/m and 25 °C and was confirmed by FTIR spectroscopy. The number of layer was 4, and the ratio of PAAS and CN-11-M was variable. Antiparallel cells were made to measure the pretilt angle of LC by crystal rotation method. The pretilt angle increased with the amount of CN-11-M, but showed a maximum.

[1] V. Percec and M. Lee, Macromolecules, 24, 4963 (1991)

ORIENTATIONAL STRUCTURES IN CHIRAL NEMATIC LIQUID CRYSTALS FOR WEAK ANCHORING, T.Beica, S.Frunza, R.Moldovan, and D.N.Stoenescu, Institute of Physics and Technology of Materials, Bucharest-Magurele CP MG 7 R-76900, ROMANIA.

This work presents a unitary mode to describe orientational structures of extreme free energy for unidimensional distortions of a chiral nematic layer with weak tilted anchoring at limiting surfaces, using structure parameters. The case of an applied electric field was also considered. A generalised expression for surface energy involving both polar and azymuthal deformations was introduced. A classification of possible structures having monotonous or non-monotonous variations of the tilt angle is presented. The solving of the equation system that links the structure parameters in each case is given.

**B4P.08** 

MEASUREMENT OF UNIFIED ANCHORING ENERGY IN A TWISTED NEMATIC CELL WITH POLYIMIDE LANGMUIR-BLODGETT FILMS

Michiyosi Kuze, Akihiko Sugimura, and Ou-Yang Zhon-can\*, Department of Information Systems Engineering, Osaka Sangyo University,\*Institute of Theoretical Physics, Academia Sinica.

We report a new experimental result for the dependence of the unified anchoring energy, which is rigorously shown in Ref. [1], between 4-pentyl-4'-cyanobiphenyl and polyimide Langmuir-Blodgett (PI-LB) substrates in the range of < 10nm. The twisted structure of substrates with weak anchoring can induce a deviation of the directors at the surfaces from an easy axis and that the anchoring energy can be evaluated by measuring pretwisted angle  $\phi^{\circ}$ . The optical retardation R dependent on  $\phi^{\circ}$  of liquid crystal (LC) cell can be determined easily by analyzing the optical transmission that passes through a LC cell and Babinet-Soleil conpensator. Still more, we have obtained the relationship between R and  $\phi^{\circ}$  by calculating the beam intensity and phase difference of optical transmission. The value of  $\phi^{\circ}$  for each LC cell can be determined by comparing the measured value of R with the calculated relationship between  $\phi^{\circ}$  and R. Unified anchoring energy increases and saturates with increasing a PI-LB film thickness.

[1] A. Sugimura, G. R. Lukhurst and Z. Ou-Yang, Phys. Rev. E 52, 681(1995)

B4P.09

A STUDY OF RELATIONSHIP BETWEEN THE PRETILT ANGLE AND THE POLAR ANCHORING STRENGTH IN NEMATIC LIQUID CRYSTAL ON RUBBED POLYIMIDE SURFACES, <u>D.-S. Seo</u> and S. Kobayashi<sup>10</sup>, Department of Electrical Engineering, Soong Sil University, 1-1, Sangdo 5-dong, Dongjack-ku, Seoul 156-743, Korea.

\*) Division of Electronic and Information Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184, Japan.

In this paper, we have investigated the effect of high pretilt angle on the polar(out-of-plane tilt) anchoring strength of the nematic liquid crystal (NLC), 4-cyano-4'-n-penthlgiphenyl(5CB), on rubbed polyimide (PI) surfaces containing trifluoromethyl moieties. The pretilt angle of 5CB rapidly increases up to about 45° with the rubbing strength (RS)[1]. Also, the polar anchoring energy of 5CB initially increases with RS for weak rubbing and then decreases. From the these result, we determined the relationship between the pretilt angle and the anchoring stength on rubbed PI surfaces. We suggest that the polar anchoring strength of 5CB with a high pretilt angle is very small because of the combination of the micro-surface excluded volume effect and the van der Waals interaction between the LC molecules and the substrate surface on weakly rubbed PI surfaces containing trifluoromethyl moeities.

A STUDY OF THE ODD-EVEN EFFECTS OF RUBBED POLYIMIDE LANGMUIR-BLODGETT SURFACES WITH ALKYL CHAIN LENGTHS ON THE POLAR ANCHORING STRENGTH IN NEMATIC LIQUID CRYSTAL, D.-S. Seo, C.-H. Lee, M. Nishikawa\*, and S. Kobayashi\*, Department of Electrical Engineering, Soong Sil University, 1-1, Sangdo 5-dong, Dongjack-ku, Seoul 156-743, Korea. \*) Division of Electronic and Information Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184, Japan.

In previous paper, we reported the anchoring strength of nematic liquid crystals (NLCs) on PI-Langmuir-Blodgett (LB)[1]. We have investigated that the odd-even effect of the alkyle chain length of rubbed PI-LB surfaces on the extrapolation length of 5CB has been successfully evaluated by measuring polar (out-of-plane tilt) anchoring strength. The extrapolation length of 5CB for rubbed PI-LB surfaces with even numbers is small compared with odd numbers for alkyl chain lengths of greater than 7 carbons. The extrapolation length of 5CB on rubbed PI-LB surfaces with odd numbers increases gradually as the temperature increases but tends to diverge near the cleating temperature (Tc). It is considered that the polar anchoring stength on rubbed PI-LB surfaces with an even number is strong because of relatively high surface ordering caused by more crystalline surfaces.

[1] D.-S. Seo, T. Oh-Ihe, and S. Kobayashi, Mol. Cryst. Liq. Cryst. 214, 97 (1992).

B4P.11

TEMPERATURE STABILITY OF A MAGNETICALLY-ALIGNED NEMATIC LIQUID CRYSTAL LAYER ON NON-RUBBED POLYIMIDE FILMS, <u>Hidenari Akiyama</u>, Norihiro Yoshida, Michinori Nishikawa, Yasufumi Iimura and Shunsuke Kobayashi, Division of Electronic and Information Engineering, The Graduate School of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.

Wetting and alignment properties of a nematic liquid crystal (NLC) on polymer surfaces have been of great interest on the physical and technical viewpoints. We study the desorption kinetics of NLC (5CB) adsorbed on two kinds of polyimide surfaces by observing the orientational disordering process of magnetically-aligned NLC cells. Thermal annealing of the magnetically-aligned NLC cell is conducted at specified temperature above the clearing point, and then the orientational ordering of the cell is evaluated as a function of the annealing temperature by measuring the dichroic ratio of a dye dissolved in the NLC. The measured dichroic ratios are compared with the theoretical calculations based on a diffusion theory. We estimates the activation energies of a rotational diffusion process and they are ranging from 0.6 to 0.8eV depending on the wettability of NLC on the film.

B4P.12

ARCHIMEDIAN SPIRAL PATTERNS IN HOMEOTROPIC NEMATIC SAMPLES: QUANTITATIVE ANALY-SIS AND SELECTION RULES. A. Vierheilig, Inst. of Physics, Univ. of Bayreuth, D-95440 Bayreuth Germany, J. M. Gilli, C. Chevallard, I.N.L.N., CNRS UMR 129, 1361 Rte des Lucioles, 06560, France.

In a nematic sample with homeotropic anchoring, and in presence of an in-plane rotating magnetic field, dynamical Archimedian spirals develop around vortices which connect Bloch wall interfaces of opposite chirality. The geometrical characteristics of these spirals (pitch, period etc) are quantitatively investigated in the experimental parameters space. The spiral pattern are fitted to an Archimedian form from which deviations are small. From the so obtained wavelength and rotation frequency we get also the velocity of an uncurved Bloch wall. The region of existence of spiral waves is limited for higher rotation frequencies of the magnetic field or lower field strengths by the transition to the asynchronous regime, where the director rotates at lower frequency than the external field and the Bloch wall interface is no longer solution.

A new model for the frequency selection of spirals has been developed to take in account the crucial role played by the size of the vortex core which is an extension of an approach proposed by Burton, Cabrera and Frank. In the case of small tilt angles of the director, measurements done on the experiments, and also done on the 2D simulations of a perturbed Ginzburg-Landau normal form (derived from the basic equations of nematics) are in good agreement with this newly derived selection model.

PECULIAR ALIGNMENT PROPERTIES OF NEMATIC LIQUID CRYSTALS WITH A BICYCLOHEXANE CORE, R. Yamaguchi and S. Sato, Akita University, Akita City, 010, JAPAN

Homogeneous alignment of nematic liquid crystals (NLCs) can usually be obtained on rubbed polymer surfaces where the molecular orientation is parallel to the rubbed direction. For example, many NLCs having a biphenyl or a phenyl-cyclohexane core and a cyano or a fluorine substituted end align parallel to the rubbing direction on a rubbed poly-hydroxyethyl methacrylate (HEMA) surface. However, peculiar alignment properties on its surface have been observed using two types of NLCs with a  $\neg(H) \neg(H)$ — core and a  $\neg(H) \neg(H)$ — core, where they align perpendicular to the rubbing direction. On the other hand, these NLCs aligned in the same direction as NLCs with the biphenyl core etc., on a rubbed polyimide surface and nonrubbed but aligning-function-copied poly-HEMA surface change from perpendicular to parallel to the rubbing direction when the NLCs are heated up to the clearing temperature ( $T_c$ ) and cooled down to the nematic phase. We have demonstrated a laser-addressing in the homogeneous cell which was composed of the rubbed poly-HEMA and the polyimide surfaces and the dye doped  $T_c \cap T_c \cap$ 

1) R. Yamaguchi and S. Sato, JJAP. 32 (1995) L897. 2) R. Yamaguchi and S. Sato, 15th IDRCI (1995) 139.

**B4P.14** 

MECHANISM OF LIQUID CRYSTAL ALIGNMENT ON POLYMER FILMS EXPOSED TO LINEARLY POLARIZED ULTRAVIOLET LIGHT, J. Chen. D.L. Johnson, P. J. Bos, X. Wang, and J.L. West, Liquid Crystal Institute and Department of Physics, Kent State University, Kent, OH, 44242, USA.

A microscopic model to elucidate the LC alignment phenomenon on polymer films exposed to linearly polarized UV light is proposed. The model successfully explains the behavior of optical anisotropy versus UV dosage. A universal relationship is predicated by the model to describe the change of the LC anchoring direction with exposure times and change of polarization direction for the case of a double linearly polarized UV exposure process. It is quantitatively confirmed by our experimental results on polyimides. Our model also successfully explains all current LC pretilt angle experimental data on linearly polarized UV exposure polymer films.

B4P.15

ALIGNMENT OF SMECTOGEN ON GROOVED SURFACE<sup>†</sup>, <u>Yushan Shi</u>, Lus J. Martines-Miranda\*, and Satyendra Kumar, Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA, \* Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD 20742, USA.

The molecular alignment in thin smectic films on a grooved surface is determined by competition between the surface tension at the free surface (air-film interface) and the elastic topological force imposed by the solid boundary. X-ray scattering studies of octylcyanobiphenyl (8CB) revealed that the homeotropic alignment resulting from the surface tension can penetrate into the grooves as the smectic layers form in solution as solvent evaporates. The homeotropic alignment inside the grooves is distorted, accompanied by topological defects when the films is heated to the isotropic phase.

† Work supported by NSF-ALCOM grant DMR-89-20147, and GER-94-50118.

NUMERICAL SIMULATION OF DIRECTOR DISTRIBUTION IN NEMATIC LIQ-UID CRYSTAL CELLS WITH WEAK ANCHORING BOUNDARIES, O. Nakagawa\*, H. Naito\*, and A. Sugimura\*\*, \*Department of Physics and Electronics, Osaka Prefecture University, Gakuencho, Sakai, Osaka 593, Japan, \*\*Department of Information Systems Engineering, Osaka Sangyo University, Nakagaito, Daito, Osaka 574, Japan

Knowledge of director distribution in nematic liquid crystal cells with weak anchoring boundaries is of crucial importance for the application of display devices. We have derived the general torque balance equations for the study of the liquid crystal cells with weak anchoring boundaries by minimizing the bulk and surface free energy simultaneously [1]. In this presentation, we report the results of the numerical calculation of the director distribution in the nematic liquid crystal cells with weak anchoring boundaries and elucidate the influence of the anchoring energy on the director distribution.

[1] A. Sugimura, G. R. Luckhurst, and Z. Ou-Yang, Phys. Rev. E 52, 681 (1995).

#### **B4P.17**

DESORPTION PROCESSES OF ADSORBED IMPURITY IONS ON ALIGNMENT LAYERS IN NEMATIC LIQUID CRYSTAL CELLS, <u>H. Naito</u>, Y. Yasuda, and A. Sugimura\*, Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka, Japan, \*Department of Information Systems Engineering, Osaka Sangyo University, 3-1-1 Nakagaito, Daito, Osaka 574, Japan.

We have studied the desorption processes of adsorbed impurity ions on varous alignment layers in nematic liquid crystal cells by measuring ac conductivity of the cells [1]. The liquid crystal used here was 4-cyano-4'-pentyl biphenyl and the adsorption of the ions was induced by the application of dc voltage to the cells [1]. Five alignment layers (three types of polyimide, polyvinyl alcohol, and indium tin oxide) were prepared. It is found in all alignment layers that the adsorbed ions decay exponentially after the dc voltage application, and that the time constants of the decay exhibit thermally activated behavior. We show that the desorption process is governed by the surface energy of the alignment layers, and discuss the underlying mechanism behind this observation.

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#### **B4P.18**

GENERALIZED TILT ANCHORING ENERGY IN LIQUID CRY-STALLINE COMPOUNDS BEARING CYANO-GROUP, V.G. Chigrinov<sup>1</sup>, A. Sparavigna<sup>2</sup>, S.I. Torgova<sup>1</sup>, and A. Strigazzi<sup>2</sup>, <sup>1</sup> Organic Intermediates & Dyes Institute, Moscow, Russia, <sup>2</sup> Dipartimento di Fisica, Politecnico di Torino, Torino, Italia

Experiments of electrically controlled birefringence were performed in very pure samples of 4-n-amyl -4'-cyanobiphenyl, 4-n-amyl -1-(4-cyanophenyl) - cyclohexane, 4-n-amyl -1-(4-cyanocyclohexyl) -cyclohexane. The aim was to obtain both threshold and saturation voltages at various temperatures in the nematic range. A model was developed, able to obtain the tilt anchoring strengths in the generalized Rapini- Papoular approach, showing the deep influence exerted by the cyclohexane ring as compared with the benzene ring.

ANCHORING TRANSITIONS IN NEMATIC LIQUID CRYSTALS WITH TWO-FOLD DEGENERATE ALIGNMENT, <u>P. Jägemalm</u>, L. Komitov, S.T. Lagerwall, B. Stebler, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Varying the evaporation angle of  $SiO_x$  aligning layers gives a continuous transition between the uniform planar orientation of nematics, with preferred direction perpendicular to the evaporation plane, and the uniform tilted one, with preferred direction lying in the evaporation plane, via a two-fold degenerate alignment with azimuthal and polar angles  $\phi$  and  $\theta$  dependent on the evaporation angle and the thickness of the  $SiO_x$  layer /1,2/. We have found that an anchoring transition, where the two preferred directions are lying symmetrically with respect to the evaporation plane, can be induced by changing the temperature. Remarkably, a large change in the azimuthal angle up to about 80° has been detected in some of the cases. Moreover, such a transition can be driven by an applied electric field. The studied anchoring transitions may have a certain potential for applications where switching of the position of the liquid crystal optic axis by temperature or by an applied electric field is required.

- 1. B.Jerome, P.Pieranski, M.Boix, Europhys. Lett., 5, 693 (1988)
- 2. M.Monkade, M.Boix, G.Durand, Europhys. Lett., 5, 697 (1988)

**B4P.20** 

FIELD EFFECT IN THE SILICON INDUCED BY A CHARGE IN THE LIQUID CRYSTAL, N.I.Gritsenko, S.I.Kucheev, Teacher's institute, 53 Sverdlova str, Chernigov, 250038, Ukraine.

It is reported that in the structure Si-NLC the following modes are possible: a) From the place where laser beam (LB) interacts with a semiconductur surface, the front of the switching director orientation and conductivity begins to spread with initial speed about  $20\mu m/s$ . The stationary size of the region with a switched orientation and conductivity (state 1) is 2 order of magnitude larger than the size of the exciting center. When LB is switched off the orientation of this region is transited (response times 1 ms) to a intermediate state 2. Keeping the written pattern goes on 10-20s. Under action of the second exciting by LB in any place of this region, a switching orientation from state 2 to state 1 is occurred (response time 700  $\mu$ s). b) If the intensity of LB is less than certain threshold, the spreading front is absent. Having been changed in the first moment under action of LB the orientation relaxes to the initial state 0 if only the light picture is stopped, but there is the vizualisation this picture if it is moving on the silicon surface. It is supposed that in the exciting center the charge storage occurs. This charge begins to spread through the LC layer and forms the charge electrod which can deplate the surface layer of a silicon.

B4P.21

EFFECT OF ELECTRIC FIELD ON PRETILT ANGLE OF LIQUID CRYSTAL MOLECULES

Xibin Shao, Ruipeng Sun, Tao Yu, Hai Jing, Sheng Wu, Ximin Huang (Changchun Institute of Physics, Chinese Academy of Sciences, P.R. China)

We have studied the effect of electric field on pretilt angle of liquid crystal molecules which was injected into the rubbed cells under certain voltage. In the experiment, the cells were fabricated with untiparallel rubbed substrates and cells' gap are about  $40\mu$  m, pure nematic liquid crystal E7 was injected into them at 65% which is a little higher than clear point, then cooled down to room temperature slowly. Certain voltage were applied on the cells during all process. As a result, we found that the molecules were aligned nearly normally to the substrate just after the electric field was turn off and changed with the time going. It reached final value after about one week. The final pretilt angle was about  $2\mu$  higher than that was obtained without applying voltage. This phenomenon would be useful for getting high pretilt angle. In the paper, we will explained it in theory.



LANGMUIR AND LANGMUIR-BLODGETT FILMS OF ASYMETRICALLY SUBSTITUTED TRIPHENYLENE DERIVATIVES, P. A. Heiney<sup>†</sup>, N. C. Maliszewskyj,<sup>†</sup> O. Mindyuk,<sup>†</sup> S. Ghosh,<sup>†</sup> J. Y. Josefowicz,<sup>†‡</sup> P. Henderson<sup>\*</sup>, U. Jonas<sup>\*</sup>, D. Beyer<sup>\*</sup>, O. Karthaus<sup>\*</sup>, and H. Ringsdorf<sup>\*</sup>. <sup>†</sup>University of Pennsylvania, Philadelphia, PA, U.S.A.; \*Johannes Gutenberg Universität, Mainz, Germany. (<sup>‡</sup>Also Hughes Research Laboratory, Malibu, CA, USA.)

We studied Langmuir and Langmuir-Blodgett films of 2,3,6,7,10,11- hexaalkoxytriphenylenes which were selectively [1] disubstituted with  $C_nH_{2n}$  — OH groups at the 2,3-, 3,6-, and 2,10-positions. At the air-water interface, the hydroxy groups make contact with the water, and the Langmuir film stability is strongly correlated with proximity of the hydroxy groups on the molecule. Mixtures of 2,3- and 3,6- isomers display an unexpected capacity for self-organization at both the air-water and air-solid interfaces. X-ray diffraction and atomic force microscopy of LB multilayer films indicate a superlattice structure of disk tilts. Infrared dichroism measurements are generally consistent with the structural results.

[1] P. Henderson et al, Liq. Cryst. 18, 191 (1995), and references therein. Supported by NSF DMR MRL 92-20668 and DMR 93-15341, and NIH RR01633.

#### B4P.23

THE APPLICATION OF PHASE TRANSITIONS IN LC VISION, M.G.Tomilin, S.I.Vavilov State Optical Institute, 199034, St.Petersburg, Birzhevaya Line 12, Russia

The thin layer of NLC applied on the surface of materials as a free film can visualize through a polarizing microscope the structural inhomogeneities and other defects [1]. We developed a new modification of this LC vision based on phase transitions in NLC. The principle idea of this technique is to use the difference in the temperature of phase transitions in NLC film applied on nondefective and defective surfaces, having different anchoring energy. Two situations are discussed. In the first case we examined MBBA film applied on the twinning growth boundary in Iceland spar. During heating one part of MBBA became isotropic while another was still in nematic phase. As the result the twinning growth boundary was visualized with absolute contrast. In the second case we observed during cooling the transition in tolans mixture from nematic to smectic B phase on the surface of LiNbO3 crystal. The small local defects were decorated by big grains of mosaic SmB structure increasing the size of defect's image. The behavior of nematic phase is explained using a simplified Landau approach.

[1] M.G.Tomilin. LC vision, Proceed of SPIE, 1993, vol.2051, pp.286-294

#### **B4P.24**

FORMATION AND X-RAY DIFFRACTION INVESTIGATION OF THIN FILMS OF LIQUID CRYSTAL 4,5' - BIS (4 - ALKYLOXYBENZOILBENZILYDENEAMINO) DIBENZO-18-CROWN -6, L.A. Valkova, L.S. Shabishev, L.A. Feigin<sup>†</sup>, Ivanovo State University, Ermak st. 39.153377. Ivanovo. Russia <sup>†</sup>Institute of Crystallography, Russian Academy of Sciences, Leninsky pr. 59, 117333, Moscow, Russia

Thin ordering films of three homologues of liquid crystal crown ethers series which have long molecules with large central part (synthesized by Akopova O.B.) were formed using LB technique [1]. It was shown, that the layer's structure on the air-water interface depends on the quantity of the matter, which was spreading on the water surface. Under the some conditions the areas occupied per molecule are too small to allow the flat molecular arrangement. The spreading data suggest an "edge on" arrangement of central cores at the water surface. The small-angle X-ray diffraction method was used in order to determine the structural properties of LB multilayer which were transfered on the solid. The results are in good agreement with the proposed model.

[1]. L.A. Valkova et al. Seventh Int. Conf. on Organized Molecular Films, Ancona, Italy P-1.15(1995) \*Supported by Russian FFI Grant 96-02-19036 and internation programm "OMMEL"

HOMEOTROPIC ALIGNMENT OF SMECTIC A PHASE - FORMATION OF A MACRO-SINGLE CRYETAL MAT, <u>Shinichi Yano</u>, Takashi Kato and Tetsuya Asano, Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

As is well known, liquid crystalline(LC) molecules are frequently alligned on the surface of the substrate in nematic(N), smectic(S) A and C phases, resulting in the formation of a LC single crystal. This work investigates the homeotropic alignments of SA phase. We synthesized 4,4'-bis(ω-hydroxyoctyloxy)azoxybenzene [HO(CH<sub>2</sub>)<sub>8</sub>O-Φ-N(O)=N-Φ-O(CH<sub>2</sub>)<sub>8</sub>OH] (HOAB), which shows phase transitions of K-(384K)-SC-(396K)-SA-(411K)-N-(414K)-I. Homeotropic alignments for HOAB were investigated for three types of cell plates whose surface was treated by NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>3</sub>SiO(CH<sub>3</sub>)<sub>3</sub> (SH6020), CH<sub>3</sub>(CH<sub>2</sub>)<sub>16</sub>CH<sub>2</sub>Si(OCH<sub>2</sub>H<sub>5</sub>)<sub>3</sub>(ODS-E), and not treated, respectively. In both the SH6020-treated and non-treated cells, interestingly, a homeotropic single crystal mat was uniformly constructed until a thickness of more than 1000μm in the SA phase and 50-100μm in the N phase, respectively, while in the ODS-E-treated cell, only until 50μm in the SA phase and not at all in the N phase. Moreover, a homeotropic SA single crystal mat of more than 1000μm thick was obtained in the non-treated cell. It is emphasized that in the homeotropic SA single crystal mat with 1000μm thick, 3 x 10<sup>3</sup>HOAB molecules are uniformly aligned perpendicular to the cell plate.

**B4P.26** 

SURFACE ANISOTROPY - INDUCED LINEAR ELECTROOPTIC EFFECT IN A NEMATIC LIQUID CRYSTAL\*, <u>Daeseung Kang</u> and Charles Rosenblatt<sup>‡</sup>, Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106 USA

A liquid crystal cell treated for homeotropic alignment with different surfactants at the two surfaces was subjected to an electric field E in the plane of the cell. The differential optical retardation  $\delta\alpha$  was found to be linear in field over a frequency range  $10 < \omega < 100~000~s^{-1}$ , where  $d(\delta\alpha)/dE \propto \omega^{-1}$ . A model is proposed which explains this result, and facilitates the determination of the anchoring strength coefficient W.

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‡ E-mail address: cxr@po.cwru.edu

**B4P.27** 

LANDAU-DE GENNES THEORY OF THE CHEVRON STRUCTURE IN A SmC LIQUID CRYSTAL CELL, N. Vaupotič\*, S. Kralj\*, M.Čopič\*, T.J. Sluckin+, \*Dept. of Physics, Faculty of Education, University of Maribor, Maribor, Slovenia, \*Dept. of Physics and Jožef Stefan Institute, University of Ljubljana, Ljubljana, Slovenia, +Dept. of Mathematics, University of Southampton, Southampton, United Kingdom.

The covariant form of the Landau - de Gennes free energy is used to study the chevron structure in a surface stabilised cell with planar boundary conditions. The chevron structure is studied in dependence of the liquid crystal elastic properties, temperature and the surface orientational anchoring strength. We show that the bistability of the chevron structure results from the continuity of the molecular director over the chevron tip of finite width and is strongly dependent of the surface orientational anchoring. We estimate analytically the threshold temperature for the chevron formation and show that above this temperature the bookshelf geometry is stable. We show that the energy of the chevron interface follows a power law dependence on reduced temperature with the exponent of 1.52±0.2.



SMECTIC FILMS AT THE AIR-WATER INTERFACE, H. Baltes, G. Brezesinski, C.A. Helm, E. Scalas, M. Schwendler, B. Struth, Dept. of Physical Chemistry, Univ. Mainz, D-55099 Mainz, Germany, M. Graeber, H. Gruler, P. Schmitz, Dept. of Biophysics, Univ. Ulm, D-7900 Ulm, W. Bouwman, K. Kjaer, Physics Dept., Riso National Laboratories, DK-4000 Roskilde, Denmark

HOBACPC (*P-Hexyloxybenzyliden-p'-amino-2-chloro-a-propylcinnamate*) is investigated at the air-water interface by means of X-ray reflection, X-ray grazing incidence diffraction and pressure-area isotherms. Lateral compression of a monolayer leads to several collapses at areas in the relation 1:1/2:1/3:1/4. X-ray reflection confirms the formation of multilayers with a constant thickness increase of 25.5Å per layer. From molecular modeling of HOBACPC we conclude, that the molecules do not interdigitate. HOBACPC has a high tendency to crystallize, which is reflected in the formation of hexatic domains at lateral pressures as low as 1.1 mN/m. According to the high intralayer interactions the structure of the resulting oblique lattice is nearly independent of the lateral pressure and of the number of layers.

## B4P.29

NEW FEATURES OF TWO-DIMENSIONAL SOFT MATTER DOMAINS: DIPS AND QUASI-CUSPS, P. Galatola and J. B. Fournier\*, Dipartimento di Fisica, Politecnico di Torino, I-10129 Torino, Italy; Laboratoire de Physique des Solides, Université Paris-Sud, F-91405 Orsay, France.

The equilibrium shape of crystals can be obtained with a simple geometrical construction introduced by Wulff. Singularities such as facets and cusps can appear: facets are an expression of the positional order, whereas cusps result from strong anisotropies linked to the orientational order. Two-dimensional mesophases of "soft matter," such as Langmuir monolayers, also present anisotropic surfaces energies. It has recently been shown experimentally that they exhibit kinked domain shapes with "virtual boojums" textures [1]. Here we theoretically determine their equilibrium shapes using a generalized Gibbs-Thomson equation [2]. We obtain kinked domains whose scaling behavior agrees with that experimentally observed, predicting new shape features characteristic of soft matter: dips and quasi-cusps. We conclude that soft matter exhibits two antagonistic trends: it gives rise to kinks even for very small anisotropies, due to the appearance of virtual textural defects, and it avoids true sharp singularities thanks to the softness of its bulk.

- [1] S. Rivière and J. Meunier, Phys. Rev. Lett. 74, 2495 (1995).
- [2] P. Galatola and J. B. Fournier, Phys. Rev. Lett. 75, 3297 (1995).

#### **B4P.30**

OPTICAL SURFACE GUIDED WAVES IN CHIRAL LIQUID CRYSTAL FILMS, V.A.Belyakov, L.D.Landau Institute for Theoretical Physics, Kosygin str.2, 117334 Moscow, Russia

Excitation and propagation of optical surface guided waves (SGEW) in chiral liquid crystals (CLC) are theoretically examined in the framework of dynamical diffraction theory [1] and an overview of the recent results in the field are presented (The SGEW are due to a total internal reflection at the boundary and diffraction scattering of light in the CLC bulk). Unusual polarization properties and propagation diagram of SGEW are discussed. In the general case the polarization properties of SGEW correspond to elliptical polarizations and are dependent on the SGEW propagation direction orientation relative to the director at the CLC surface, the SGEW frequency and the film thickness [2]. A qualitative difference related to the excitation and attenuation of SGEW in semi-infinite CLC and CLC films exists. The SGEW attenuation does not vanish even in nonabsorbing CLC films if total internal reflection (TIR) at one of the film boundaries is absent. SGEW excitation by a beam incident at the film boundary without TIR [3] is investigated. The mentioned SGEW properties are illustrated by the calculations.

[1] V.A.Belyakov, Diffraction Optics of Complex-Structured Periodic Media, N.Y., Springer Verlag, 1992. [2] V.A.Belyakov, G.I.Shilina, Phys. Chem. Mech. Surf., v.10 (n2), p. 155 (1995). [3] V.A.Belyakov, Proc. SPIE 237, p.123 (1995).

# BIAXIAL NEMATIC AND SMECTIC A BOUNDARY LAYERS IN THIN PLANAR SAMPLES OF 80CB ALIGNED BY RUBBED POLYIMIDE.

Francis Beaubois and Jean-Paul Marcerou, Centre Paul Pascal CNRS, F-33600 PESSAC.

henvl) samples, has been measured The birefringence of planar 8OCB (octyloxyc as a function of temperature for thicknesses 7.2 to 2.6 µm. The first curve (at opic measurement done with a 100 μm 7.2 µm) is perfectly superimposable to Withdrawn thick homeotropic uniaxial same a minimum value of 0.08 close to the isotropic phase up to a plateau ne smectic A phase. For thinner planar samples, one (up to 35% more in both phases with a new plateau at 0.26). recovers an increar consider that the bulk uniaxial phase is surrounded by biaxial (nematic This means that one or smectic A) boundary layers where the largest and the smallest indices of refraction lie parallel to the plates. These layers are created by a long range interaction (a few µm in the normal direction) with the rubbed polyimide surfaces.

**B4P.32** 

TEMPERATURE DEPENEDENCE OF NEMATIC ANCHORING ENERGY ON WEAK SURFACES OF POLYIMIDE LANGMUIR-BLODGETT FILMS, Y. Peng\*, T. Miyamoto,\* H. Naito\* and M. Kuze\*\*, A. Sugimura\*\*, \* Department of Physics and Electronics, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 593, Japan, \*\* Department of Information Systems Engineering, Osaka Sangyo University, Nakagaito, Daito, Osaka 574, Japan.

We have developed a theory for a twisted chiral nematic liquid crystal (TN) cell with weak anchoring boundaries, and have stressed the importance of the unified anchoring energy concept [1]. Within the framework of the theory, the expression for the threshold and the saturation field have been derived. In this presentation, we report the determination of anchoring energy at 4-pentyl-4'-cyano biphenyl/polyimide Langmuir-Blodgett alignment layer interface by measuring the saturation field of the TN cell. We find that the anchoring energy is of the order of  $10^{-6}$ J/m<sup>2</sup> and decreases with increasing temperature toward the nematic-isotropic point.

[1] A. Sugimura, G. R. Luckhurst and Z. Ou-Yang, Phys. Rev. E 52, 681 (1995)

**B4P.33** 

A FIELD-OFF CORRELATIONAL METHOD FOR MEASURING THE AZIMUTHAL ANCHORING ENERGY OF CHOLESTERIC LIQUID CRYSTALS AT ISOTROPIC OR ANISOTROPIC INTERFACES, T. M. Martin and J. L. West, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

We report a new transmissive method to estimate the azimuthal anchoring energy at a cholesteric liquid crystal-solid material interface. This method can be used to determine the azimuthal anchoring energy even at a wide variety of interfaces, including isotropic media. We correlate the rate at which a cholesteric liquid crystal returns to the planar state from the homeotropic state with the azimuthal surface energy. Elementary calculations and use of Faetti's method allow the azimuthal surface energy to be determined at any liquid crystal interface. We report preliminary measurements.

<sup>&</sup>lt;sup>1</sup> S. Faetti, V. Palleschi, and A. Schirone, Il Nuovo Cimento. 10, 1313 81988).

SURFACE TOPOGRAPHY OF CHIRAL SMECTICS BY AFM, M.Thieme, A. Hauser, and A. Saupe, Max Planck Research Unit Liquid Crystalline Systems, Mühlpforte 1, D-06108 Halle / S., Germany

The modulation of free surfaces can give important information on the molecular structure of liquid crystals and on defect structures. The topography of glassy states can be studied in high resolution by atomic force microscopy. We studied MHPOBC, a chiral material which has a sequence of smectic phases, starting from A, followed by 4 types of chiral C phases and an I phase [1]. Samples were prepared by spreading the material on a glass plate at an elevated temperature and cooling them rapidly to the glassy state at room temperature or, alternately, by removing the cover plate of a sandwiched film after cooling to the glassy state. The surfaces showed in general a strong modulation which is related to the microscopically observed textures. Fan textures are connected with a strong modulation in which helical structure is also reflected so that the pitch can be directly measured. Circular focal conic domains are connected with funnel shaped dips in the center. Such dips can also be seen with an interference microscope. The surface obtained by removing the cover plate showed very different patterns. We observed domains of curved stripes with a secondary modulation that gave them the appearance of a string of pearls. This pattern belongs probably to a not yet described lower temperature phase that also has a helical structure.

[1] K. Hiraoka, Y. Takanishi, K. Skarp, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. 30, L1819 (1991)

**B4P.35** 

A NEW METHOD OF MEASURING SURFACE TORSIONAL ANCHORING STRENGTH FOR NEMATIC LIQUID CRYSTALS, <u>T.Akahane</u>, H.Kaneko and M.Kimura, Department of Electrical Engineering, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka 1603, Nagaoka, Niigata 940-21 Japan

We have proposed a simple and accurate method of measuring surface torsional anchoring stength for nematic liquid crystals. This method is based on the simultaneous determinations of the actual twist angle and the cell gap (optical retardation) of a twisted nematic cell where the easy axes of upper and lower substrates make a definite angle  $(e.g.\ 90^\circ)$ . The TN cell is placed between two polarizers. The TN cell and the analyzer are mounted on rotatable stages. The process of the measurements are; (1) Using a monocromatic light, we minimize the light transmission by rotating both the TN cell and the analyzer (we put the angles of the analyzer and the TN cell from the polarizer as  $\Psi_p^{(1)}$ , and  $\Psi_0^{(1)}$ , respectively. (2) We fix the TN cell at a definite angle from  $\Psi_0^{(1)}$ , and minimize the light transmission by rotating only the analyzer (we put the angle of analyzer as  $\Psi_p^{(2)}$ ). From the values of  $\Psi_p^{(1)}$  and  $\Psi_p^{(2)}$ , we can determine both of the actual twist angle and the optical retardation using the analytical expression of optical transmissivity based on the Jones matrix method. We discuss the accuracy of this method. Examples of the experiments are also shown.

**B4P.36** 

ORIENTATIONAL DYNAMICS AND PHASE TRANSITION IN THE SURFACE LAYER OF A LYOTROPIC LIQUID CRYSTAL, E. A. Oliveira<sup>1</sup>, V.L. Lorman<sup>2</sup>, and B. Metout<sup>3</sup>, <sup>1</sup>Instituto de Fisica, Universidade de São Paulo, P.O.Box 66318,CEP 05389-970,São Paulo-Brazil, <sup>3</sup>Laboratoire de Physique des Solides, ESPCI-CNRS, 75231 Paris, Cedex 05, France.

It has been shown that lyotropic liquid crystals exhibit two types of orientation process when an external magnetic field H is applied, the first one with a response time  $\sim$ 10s related to the orientation of the director in the bulk and a slow one,  $\tau\sim$ 10<sup>3</sup>s and proportional to  $1/H^2$ . We present in this work, a theory to describe the dynamic behaviour of the surface layer of lyotropic liquid crystals using Landau-Khalatnikov equations. Due to the anchoring of the micelles at the surface, a biaxial interface is formed between the solid substrate and the uniaxial nematic in the bulk. The direct interaction of the biaxial interface of finite thickness with the magnetic field leads to the orientation process with inverse characteristic time proportional to  $H^2$ . Decreasing the temperature through the sequence of calamitic-biaxial-discotic transitions in the bulk induces orientational phase transition in the interface with qualitative changes in the dynamic behaviour.

<sup>&</sup>lt;sup>2</sup>On leave from Université de Picardie, Amiens-France

# MOLECULAR ORIENTATION OF LIQUID CRYSTALS PHOTOREGULATED BY 'COMMAND SURFACES' STUDIED BY RAMAN AND INFRARED SPECTROSCOPY

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Alignment behaviors of liquid crystals (LCs) by the surface molecular layer structure 'Command Surfaces' have long been a matter of active investigations. We have performed Raman and infrared spectroscopic study on molecular orientation for two sorts of LCs photoregulated by Langmuir-Blodgett films of azobenzene-poly (vinyl alcohol) derivatives. The present study provides the following conclusions for the reorientation of LCs: (i) polarized Raman spectra of the LCs in isotropic, planar, and homeotropic orientation show intensity changes on dominant bands; (ii) yet DON-103 is superior to cyanobiphenyls (nCB) in degree of reorientation, infrared study: demonstrates the orientation and anisotropy of these LCs in molecular segment level; (iii) length of hydrocarbon chain of nCB is influential in the reorientation behavior.

**B4P.38** 

A STUDY ON SURFACE TOPOGRAPHY OF RUBBED POLYIMIDE FILMS FOR LIQUID CRYSTAL DISPLAYS BY SCANNING FORCE MICROSCOPY, Y. B. Kim, B. S. Ban and H.Olin\*, Department of Chemistry, College of Science, Kon-Kuk University, Seoul 133-701, Korea, \*Department of physics, Chalmers University of Technology, S-41296 Goteborg, Sweden

Rubbed polyimide films are widely used for achievement of uniform alignment in liquid displays. Although studied for a long time, the alignment mechanism on such films is still not clear. Here, we compare the surface structure of rubbed polyimide films as directly observed by SFM(scanning force microscopy) and discuss their aligning properties. The polyimide (AL-1051 and AL-8044 type, JSR Co. Ltd.) films were printed on ITO glass substrates. Rubbing was done with a nylon velvet. Standard Si<sub>3</sub>N<sub>4</sub> SFM tips were used in a commercial SFM. The surface of the unrubbed polyimide films consists of randomly oriented polymer chains distributed in clusters on a scale much larger than the individual molecules. The surface topography is drastically changed after rubbing: the clusters are now aligned along the rubbing direction and form systems of long rows and grooves. Moreover, the polymer chains within the clusters attain a degree of order. Two different systems of rows overlapping each other can he distinguished. For higher rubbing strength it is found that the fine rows become wider. The degree of the polymer chain orientational order was also estimated by measuring the optical retardation of the rubbed films using the Senarmont method.

**B4P.39** 

ATR-IR SPECTROSCOPY STUDY OF NLC ORIENTATION AT THE PLASMA-POLYMERIZED LAYERS SURFACE, A.I. Vangonen and E.A. Konshina\*, All-Russia Science Center S.I. Vavilov State Optical Institute, St. Petersburg, 199034, Russia.

The parallel and perpendicular polarized Multiple ATR -IR spectra in the range of 4000-900cm<sup>-1</sup> of the thin nematic layers (200-600nm) have been investigated The alkylcyanobiphenyls LC mixture with positive dielectric anisotropy was defined. For achievement of a planar alignment has been used amorphous hydrogenated carbon (a-C:H) layers [1] produced from benzene by plasma-activated chemical vapors deposition process in glow discharge on direct current. Homeotropic alignment has been achieved by means plasma-polymerized octane (PPO) layers. The dichroic ratio for C-H stretching at 2920 cm<sup>-1</sup>, C=N stretching at 2220 cm<sup>-1</sup>, the phenyl C-C stretching at 1600-1500cm<sup>-1</sup> were calculated. The models of the interaction mechanism of the LC with a-C:H and PPO layers in the absence of external fields to explain the results are proposed.

[1] E.A.Konshina, Crystallography 40, N6, 1074 (1995). \*Supported by ISF Grant NXQ300.

BROKEN SYMMETRY AT THE LIQUID CRYSTAL-PTFE ALIGNING LAYER INTERFACE, M. Brunet, G.D.P.C., Université Montpellier II, F34095 Montpellier Cedex 05, France.

Thin films of Teflon, obtained by simple friction at high temperature on glass plates have a remarkable degree of organization and thus the property of aligning some polymers and nematics. With a good choice of the temperature, pressure and friction speed, very well aligned liquid crystal samples can be obtained. However, using this method to aligne chiral smectics, we have observed that changing the parameters of the deposit leads to a deviation for the smectic layers from the expected direction which is the normal to the friction direction.

To find the cause of this phenomena we selected several pure chiral and non chiral liquid crystals, displaying various sequences of phases and we observed the textures and defects between crossed polarizers, from the isotropic phase to the last mesophase before the crystallisation. These observations will be described from photographs: the direction of the smectic layers, the angle of extinction and its variation in relation with the temperature, the succession of the textures during the transitions and the connection they have between them. Teflon induces a breaking of symmetry on the surface. The effect in the bulk is induced by the surface interaction and is dependent of the sequence of phases. Some causes can be evoked for these effects: they will be discussed.

# B4P.41

INVESTIGATION OF SUBSTRATE'S SURFACE INFLUENCE ON DISCOTIC LIQUID CRYSTALLINE ALIGNMENT USING INFRARED SPECTROSCOPY. T.S. Perova<sup>+</sup>, and J.K. Vij\*.

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Previous IR measurements [1] of discotic liquid crystals have shown that aromatic vibrations (1600-1500 cm<sup>-1</sup>) as well as the C-H aromatic out of plane vibrations near 800-850 cm<sup>-1</sup> are the most sensitive indicators of the ordering in liquid crystalline materials. A relatively large value of the order parameter (~0.85-0.6) for the aforementioned bands has been found in measurements for hexa-n-pentyloxytriphenylene (H5T) enclosed between two Si windows [1]. The "side-on" type of alignment has been proposed for the case in [1] since the intensity of vibrations with transition dipole moment lying in the plane of the core are higher in the discotic phase than in the isotropic phase. Our present investigations show that when H5T is enclosed between two ZnSe windows the type of alignment is different to those for the Si windows. For this case the alignment is "edge-on" or approximately "edge-on". A strong influence of the substrate's structure on the alignment of discotic liquid crystals has also been demonstrated from the analysis of infrared data for hexa-n-decanoyloxytruxene.

G. Kruk, A. Kocot, R. Wrzalik, J.K. Vij, O.Karthaus and H.Ringsdorf, Liquid Crystals, 1993, 14, 807.

#### **B4P.42**

SURFASE MEMORY EFFECT IN NEMATICS WITH SMECTIC C SHORT -RANGE OR-DER AND HYDROGEN BONDED MOLECULES, M. P. Petrov and L. V. Tsonev, Institute of Solid State Physics "G. Nadjakov", Bulgarian Academy of Sciences, 72 Tzarigradsko chaussee blvd., 1784 Sofia, Bulgaria

Surface memory effect (SME) is found in the dimerized nematic with short range smectic C order - 4,noctyloxybenzoic acid (OOBA) in a cell which walls had been covered with an obliquely evaporated SiO or ITO layer. The recording and erasure processes are discussed and the erasure in the nematic phase is realized for the first time. Recording of several images in one and the same cell, where they exist simultaneously is realized. We prooved that in our cell (the combination of liquid crystal substance OOBA and cell wall's covering SiO or ITO) there is a strong anchoring, which stimulates the stability of the recorded textural image. Analyzing the recording process (by dynamic erasure) we conclude that the surface memory effect in our case is a strong one and it has a large thermal sensitivity. A mechanism for the surface memorizatin is presented, which takes into account the specific character of the dimerized nematics preceding upon cooling smectic C phase.

THERMOSTABLE TILTED ALIGNMENT OF A NEMATIC LIQUID CRYSTAL AT A POLYMER SURFACE EXPOSED TO UV-LIGHT AND A MAGNETIC FIELD\*. Yu. A. Reznikov<sup>a</sup>, R.G. Petschek, and C. Rosenblatt, Dept. of Physics, Case Western Reserve Univ., Cleveland, Ohio 44106 USA and <sup>a</sup>Inst. of Physics, Nat. Acad. of Sciences, Prosp. Nauki 46, Kyiv 252022 Ukraine

As homogeneous alignment of liquid crystals is necessary for normal operation of LC displays, the development of new methods of alignment is of great importance. A promising new alignment technique involves a polymer film, which aligns anisotropically when exposed to UV light [1,2]. Wide use of this photoalignment technique is hampered, however, by both low thermostability of the pretilt and its two-fold degeneracy. To circumvent these problems we have developed a modified technique which involves UV exposure of a filled LC cell in the presence of an aligning magnetic field. We find that the pretilt angle of the director can be high (~15°), and that this pretilt is quite robust over long periods of time and at elevated temperatures (100°C).

- [1] M. Schadt, K. Schmidt et al, Jpn. J. Appl. Phys. 32, 2155 (1992).
- [2] T. Marusii and Yu. Reznikov, Mol. Mat. 3, 161 (1993).
- \* Supported by ISF grant U5W000 and by NSF grants DMR-9502825 and DMR-8920147

**B4P.44** 

A SIMPLE AND RELIABLE METHOD FOR MEASURING THE ANCHORING STRENGTH COEFFICIENT\*, Dong-Feng Gu<sup>‡</sup>, S. Uran, and <u>Charles Rosenblatt</u>, Dept. of Physics, Case Western Reserve University, Cleveland, Ohio 44106 USA

By measuring the electric Freedericksz transition threshold in a wedged capacitance cell, we have developed a simple method for determining the anchoring strength coefficient for tilt of the director relative to the substrate normal [1]. This technique requires neither a knowledge of the absolute cell thickness nor a knowledge of the optical birefringence. Moreover, it applies to both the homeotropic orientation for  $\Delta \chi < 0$ , and to the planar orientation for  $\Delta \chi > 0$ , where  $\Delta \chi$  is the dielectric susceptibility anisotropy.

[1] D.-F. Gu, S. Uran, and C. Rosenblatt, Liq. Cryst. 19, 427 (1995)

† Present address: Rockwell Corp. Science Center, Thousand Oaks, California 91358 USA

**B4P.45** 

DISCONTINUOUS BULK REORIENTATION INDUCED BY CONTINUOUS EVOLUTION OF SURFACE ORDER,

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We have studied the effect of water vapor on the orientation (or anchoring) of cyanobiphenyls on phlogopite mica whose surface exhibits a three-fold symmetry. We have determined, on the one hand, the molecular orientational distribution at the surface (by optical second harmonic generation) and on the other hand, the orientation of the bulk director (with a polarizing microscope). With increasing partial water vapor pressure, the macroscopic anchoring direction of the liquid crystal changes discontinuously while the surface orientational distribution evolves continuously. Moreover the bulk in-plane reorientation is correlated to a change in molecular tilt distribution at the surface, while the surface in-plane preferred orientations remain unchanged. These observations can be explained by the fact that the surface molecular ordering is not nematic-like because of the high symmetry of the phlogopite mica surface. The bulk orientation arises from a coupling between this highly symmetric order and the uniaxial nematic order which appears as one moves away from the surface. This coupling can be described using an extended version of the Landau-de Gennes theory.

<sup>\*</sup> Supported by the NSF's Advanced Liquid Crystalline Optical Materials Science and Technology Center under grant DMR-8920147

SURFACE ANCHORING STRENGTHS OF NEMATIC LIQUID CRYSTALS FROM MOLECULAR DYNAMICS SIMULATIONS<sup>†</sup>, <u>J. Stelzer</u>, L. Longa, and H.-R. Trebin\*, Instytut Fizyki, Uniwersytet Jagielloński, Kraków, Poland, \*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Germany.

The surface anchoring strengths  $W_2$  and  $W_4$  for homeotropic surface anchoring have been calculated for a model liquid crystal from molecular dynamics simulations. The molecular pair interactions were evaluated from the Gay-Berne potential. The surface was modelled by a one-particle potential derived from the Gay-Berne interaction that favours alignment of the molecular axes along the surface normal. — For the derivation of the surface anchoring strengths from the molecular dynamics data we established a direct correlation function approach according to the functional expansion of the free energy up to pair correlations. Apart from expansion coefficients of the direct correlation function, our expressions for the surface anchoring strengths depend on generalized order parameters and on the surface-induced layering, which have been taken directly from the simulation data. We shall discuss the temperature dependence of the surface anchoring strengths and of the surface-induced layering.

† Work supported by the Deutsche Forschungsgemeinschaft under grant No. Tr 154/7-2.

#### **B4P.47**

# CRITICAL PROPERTY OF SURFACE ANCHORING ENERGY FOR LIQUID CRYSTALS Ruipeng SUN, and Ximin HUANG

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The surface azimuthal anchoring energy for liquid crystals can be obtained by measuring the twist angle in the twist cell and the surface torsional angle between the rubbing direction and the liquid crystal director at the substrate boundary[1]. The temperature dependence of surface anchoring energy at 5CB-polyimide (PI) interface was studied. The surface anchoring energy decreases with increasing the temperature from  $5.0 \times 10^{-5} \text{J/m}^2$  at 25.5 °C to  $5.0 \times 10^{-6} \text{J/m}^2$  at 35.0°C. This result clearly signifies the important role of the ordered structure of the nematic interface in determining the temperature dependence of the anchoring strength at the 5CB-PI interface.

[1] Ruipeng SUN, Ximin HUANG, et al., Phys. Rev. E, 58, 1253 (1994)

#### **B4P.48**

SURFACE DEFECTS AND FORCES IN NEMATIC LIQUID CRYSTAL SAMPLES, F. C. Cardoso and L. R. Evangelista, Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, Paraná, Brazil.

The existence of surface defects resulting from the inhomogeneity of the surface treatment in a nematic liquid crystal sample of definite thickness is investigated. We consider two significant experimental arrangements for the flat surfaces, in the hypothesis of strong and weak anchoring. By means of a theoretical model, the force between the surface defects is analytically determined. The forces are shown to have a non-linear dependence on the relative displacement between the defects. An analytical expression connecting the force and the anchoring strength is also presented.

ANCHORING ENERGY AND TEMPERATURE HYSTERESIS OF THE PITCH JUMP POINT IN PLANAR CHOLESTERIC LAYERS, H. Zink, Laboratorium voor Akoestiek en Thermische Fysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium V.A. Belyakov, L.D. Landau Institute of Theoretical Physics, Kosyginstr. 2, 117334 Moscow, Russia.

Analysis of the temperature dependence of the optical characteristics [1] of planar oriented CLC - layers [2], shows that just before the change of the number of half-pitches within the layer thickness by one, the director direction at the surface essentially differs from the alignment direction and the jump temperature is dependent on the direction of the temperature change. The observed hysteresis and the deviation angle are dependent on the force of the molecular anchoring at the surface and therefore the measurements can be used to obtain information about the anchoring forces. Measurements of the jump point temperature hysteresis, are presented and discussed in the framework of the conventional theory of CLC elasticity incorporating the surface anchoring forces. The angle of the director deviation is calculated and the hysteresis parameters are estimated for various mechanisms of the director configuration change at the pitch jump point and compared with the measured values. The value for the Rapini-Popular anchoring potential is found for the samples used in the measurements

[1]V.A.Belyakov,Diffraction Optics of Complex Structured Periodic Media.(Springer Verlag, N.Y., 1992) [2]H.Zink,V.A.Belyakov,Mol.Cryst.Liq.Cryst.V265,445 (1995); JETP Lett.V63 (1),37 (1996), (russian edition)

**B4P.50** 

PREPARATION AND CHARACTERIZATION OF LB FILMS OF DIAZA-CROWN ETHER CARRYING TWO CHOLESTERIC UNITS, Li Tian-Kai\*, Xu Jing-Mei\*, Zhao Wei\*, Jiang Qing\*, Xie Ming-gui\*, \*Institute of Photographic Chemistry, Academia Sinica, Beijing, 100101, CHINA; \*Department of Chemistry, Sichuan University, Chengdu, 610064, CNINA.

Monolayer of diaza-crown ether double-armed with cholesteric units was prepared and the surface pressure-area curve showed its good and stable film characterization. The case is altogether diffrent from the experimental results of its monoarm liquid crystalline crown ether [1]. UV absorption spectra and low-angle diffraction pattern of multilayers suggested that monolayers could be easily transferred onto substrates to form well-organized layered structure with each layer having the same uniform thickness of 2.6nm. Relating to CPK atomic model, the molecular configuration in LB films was speculated.

[1] Jiang Qing, Zhao Wei, Li Long-Zhang, Hu Zi-Lun, Xie Ming-Gui, Zhu Yang-Ming. and Lu Zu-Hong, YOUJI HUAXUE (CHINESE JOURNAL OF ORGANIC CHEMISTRY), 15, 604 (1995).

B4P.51

SURFACE INTERACTIONS OF LIQUID CRYSTALS CONFINED IN NUCLEPORE MEMBRANE

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Nuclepore membranes are polycarbonate films with well defined cylindrical pores. The inner surface of the pores were chemically altered with lecithin. The membranes are then permeated with the liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB). The lecithin weakens the interaction between the liquid crystal molecules and the membrane surface to induce the zero electric field planar polar configuration[1]. However, the escaped radial with point defects is the zero electric field configuration for the untreated membranes[1]. The filled membranes are then sandwiched between two conductive substrates. The threshold voltage, contrast, and switching times were determined from the electrooptical responses. The threshold voltage is inversely proportional to pore size for the untreated membranes and the threshold voltage is proportional to pore size for treated membranes.

[1]G.P. Crawford, M. Vilfan, and J.W. Doane, Phys. Rev. A43, 835 (1991).

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#### PHOTOACTIVE FREE-STANDING FILMS

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Free-standing films of mixtures of a ferroelectric C7 and an azo-dye (ethyl-phenylazo-phenyl nonylamin) are studied. In the smectic A phase temperature interval the illumination causes local heating which results in the unusual local phase transition SmA - iso in thick films. The isotropic phase droplets occur after illumination during a time interval  $\tau$ , which lineary depends on the temperature difference (T-T<sub>AI</sub>), where T<sub>AI</sub> is the transition temperature SmA - iso. This transition takes place in the films interior and the films remain mechanically stable due to the surface smectic layers. Reorientation of the optical axis of the free-standing SmC\* films under illumination with polarized light is observed. In the smectic C\* phase a stripe state is stable in thick films [1]. The configuration of the stripe texture can be changed by rotation of the polarizer at fixed illumination intensity. Both effects have some intensity threshold and depend on the illumination spectrum. Thickness and concentation dependence of the effects is studied using different dye dopants. Relevant theoretical models are discussed.

[1].E.I. Demikhov, Europhys. Lett. 25, 259 (1994); E.I. Demikhov and S.A. Pikin, JETP Lett. 61, 686, (1995); E.I. Demikhov, E. Hoffmann, S.A. Pikin et. al., Phys. Rev. E 51, 5954 (1995)

B4P.53

SMECTIC FILMS STABILITY: EDGE DISLOCATIONS AND MENISCUS, J. — C. Geminard, R. Holyst<sup>o</sup>, P. Oswald, and P. Pierànski<sup>o</sup>, Laboratoire de Physique de l'ENS de Lyon, 46, Allée d'Italie, 69364 Lyon cedex 07.

Drawing out a dropplet of smectic liquid crystal on a frame, it is easy to obtain a free-standing film. The film is remarquably stable in spite of its small thickness ( it ranges from a few molecular layers to several hundred of layers). A meniscus connects the film to the frame: We deduce experimentally its profile by measuring the local optical reflectivity. We have developed a theoretical model, taking into account the existence of edge dislocations in the meniscus, that allows us to deduce the pressure inside the film from this experimental profile: The shape of the meniscus results from the competition between the elastic effects and the surface free energy. The profile of the meniscus is circular and not exponential like it should be for an isotopic liquid for which the gravity can not be neglected. We use afterwards this measurement of the pressure in the film to estimate the line tension of the edge dislocations.

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**B4P.54** 

ELECTRON-DIFFRACTION STUDIES OF PHASE TRANSITIONS IN 40.8 FREE-STANDING THIN FILMS, C.Y. Chao, C.F. Chou, and J.T. Ho, Department of Physics, State University of New York at Buffalo, Buffalo, NY 14260, USA, S.W. Hui, Department of Biophysics, Roswell Park Cancer Institute, Buffalo, NY 14263, USA, A.J. Jin and C.C. Huang, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455, USA.

The structural phase transitions of free-standing thin films of N-(4-n-butyloxybenzylidene)-4-n-octylaniline (40.8), which exhibits smectic-A and crystal-B phases in the bulk, have been studied in detail using electron diffraction. When a smectic-A film is cooled, the outermost layer transforms initially to the hexatic-B phase and subsequently to the crystal-B phase at a lower temperature. The first transition is consistent with the thermal anomaly in the heat capacity and the second transition coincides with the shear response observed in mechanical measurements. Upon further cooling, the film undergoes additional layer-by-layer smectic-A-hexatic-B-crystal-B transitions in its interior.

SPIRAL PATTERNS, ORBITING DEFECTS AND HYDRODYNAMICAL FLOW IN SM C\* FREE STAND-ING FILMS UNDER ROTATING FIELDS, J. M. Gilli, <u>C. Chevallard</u>, T. Frisch, I.N.L.N., CNRS UMR 129, 1361 Rte des Lucioles, 06560, France, P. Pieranski, CNRS, Physique des Solides, Bt 510, Univ. Paris-Sud, 91405 Orsay Cedex, A. Vierheilig, Inst. of Physics, Univ. of Bayreuth, D-95440 Bayreuth Germany.

We apply an in plane electric rotating field on a few nm thick free standing SmC\* film. Close experiments have been done in the past on SmC films by P. E. Cladis and coll. (1) and G. Hauck and coll. (2).

The new experimental results are here:

--The observation of orthoradial hydrodynamical flows in the plane of the film associated to the winding and relaxation of the director phase. These hydrodynamical phenomena are strongly dependent on the topology of the film (presence of +1,or -1 defects).

-The observation of systems of orbiting defects, allowing for the stationary variation of the phase in the middle part of the film, in spite of the rigid boundary condition in it's external parts.

A Ginzburg- Landau model is derived to describe some of these experimental aspects

1)P.E. Cladis, P. L. Finn, H. Brand, Phys. Rev. Lett., 75, 1518, 1995, and P.E. Cladis, Y. Couder, H. Brand, Phys. Rev. Lett., 55, 2945,1985.

2)G. Hauck, H. D. Koswig, U. Labes, Liq. Cryst., 14, 991, 1993, and G. Hauck, H. D. Koswig, Mol. Cryst. Liq. Cryst., 262, 1427, 1995.

**B4P.56** 

MICROSCOPIC MODEL FOR LC ANCHORING, J. Chakrabarti and <u>B. M. Mulder</u>, FOM Institute for Atomic and Molecular Physics, Kruislaan 407, NL-1098 SJ Amsterdam, The Netherlands

Experimental observations indicate that a liquid crystal in contact with a solid substrate creates an adsorbed monolayer with a structure highly different from that of the bulk [1]. This imposed order at the substrate-LC interface decays into the bulk over a characteristic relaxation length and causes a specific anchoring angle to be selected. We have investigated the simplest microscopic model consistent with this picture of the anchoring phenomenon: a Lebwohl-Lasher lattice model with a semi-infinite geometry and fixed orientation distribution functions as boundary conditions. Using both Monte Carlo simulations and mean-field theory we discuss the anchoring phase diagram of this system as a function of the parameters describing the boundary distributions. For uniaxial boundary distributions a homeotropic-planar transition is triggered by a sign change of the surface nematic order parameter.

[1] B. Jérôme Rep. Prog. Phys. 54 391 (1991)

**B4P.57** 

SURFACE TENSION OF FREE STANDING SMECTIC FILMS, M. Eberhardt<sup>1</sup> and R.B. Meyer, Physics Dept., Brandeis University, Waltham, MA, 02254, USA, <sup>1</sup>Biophysics Dept., Ulm University, 89081 Ulm, Germany.

We developed a new apparatus for measuring the surface tension of free standing smectic films and its temperature dependence. The temperature dependence of the surface tension  $\sigma$  is much more sensitive to structural changes in the surface than  $\sigma$  itself and can be related to the surface excess entropy of the interface. There are two contributions to the excess free energy of the interface: a) entropy favors a diffuse density profile at the interface and yields to a negative slope for  $\sigma(T)$  b) interaction energy want's the surface to be sharp and for anisotropic media can also produce a torque field in the interface. Case a) produces a negative slope for  $\sigma(T)$  case b) a positive. For simple smectic liquid crystals that show only a smA phase (8CB) we find a constant negative slope. For materials showing smC or smC\* phases we find a crossover from a negative slope to a positive slope when cooling down from the smA to the smC phase. The crossover temperature is lower than the phase transition temperature. We will also discuss the effect of film thickness.

# Conditional Distribution Function Approach to the Theory of Anchoring Transitions

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A statistical-mechanical theory which takes into account the correlations between translational-translational, orientational-orientational and mixed correlations, based upon the method of conditional distribution functions, is applied to calculations of the surface free energy and anchoring transitions of a system composed of interacting ellipsoidal molecules near an interacting wall. The calculations have been carried out for cubic close packing with the nearest-neighbor Gay-Berne intermolecular potential and with a (9-3) like orientation-dependent molecule-wall interaction. The theory shows that the number of surface layers which must be taken into account depends more on the character of intercell correlations in the system than on the direct wall-nematic interaction. The equilibrium surface free energy profiles and different type of anchoring transitions at the solid-nematic fluid interface have been calculated.

B4P.59

DEFORMED SURFACE - INDUCED SMECTIC A - STRUCTURE IN NEMATIC LIQUID CRYSTAL, L. V. Mirantsev, Institute for the Problems of Mechanical Engineering Academy of Sciences of Russia, St. Petersburg, 199178, Russia

In the present report the smectic A - phase induced by the deformed substrate surface in a nematic liquid crystal is considered. The surface microrelief is described by one - dimensional harmonic function. In framework of Landau - de Gennes model the dependences of the surface smectic order parameter and the depth of penetration of the interfacial smectic structure into the nematic bulk on the amplitude and the period of the surface microrelief are obtained. It is shown that the deformation of the substrate surface gives rise to the suppression of the interfacial smectic structure. It is also investigated the effect of the interfacial smectic structure on the depth of penetration of the surface microrelief - induced deformation into the sample bulk. The possibility of experimental verification of the results obtained is discussed.

B4P.60

THEORY OF LAYER - THINNING TRANSITIONS IN FREE - STANDING SMECTIC - A FILMS

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In the present report a discrete mean - field model for thin smectic - A liquid crystal films with two boundary surfaces is offered. The model accounts for the recently observed phenomenon of layer - thinning transitions in the free - standing smectic - A films upon heating. In particular, the model predicts the observed multiple layer jumps as well as, for films thinner than 13 layers, the observed power law dependence of the layer - thinning transition temperatures on film thickness. The influence of the external magnetic (electric) field on the layer - thinning transitions is also investigated.

**B4P.61** 

STRONG ELECTRIC FIELD EFFECT ON THE ORIENTATIONAL ORDER IN LIQUID CRYSTALS, Geetha Basappa and N.V. Madhusudana, Raman Research Institute, Bangalore 560 080, INDIA.

An electric field is conjugate to the orientational order in liquid crystals because of the coupling of the field with the dielectric anisotropy of the medium. Electric field effects on NI phase diagrams have been measured only recently[1-2]. In our technique we measure the local temperature of the sample, and both the dielectric constant which depends on the orientational order and the electrical resistance which is sensitive to the smectic layering order in the medium.[2] In this paper we present results with an improved set up in which the optical path difference of the cell is simultaneously measured. We present the first results on materials with negative dielectric anisotropy and discuss the same in the framework of an appropriate Landau theory.

- [1] I.Lelidis and G.Durand, Phys. Rev. E 48, 3822 (1993); Phys. Rev.Lett 73, 672 (1994).
- [2] Geetha Basappa and N.V.Madhusudana, Int.Symp.on Liquid Crystals, Bangalore Jan 3-6 (1996).

**B4P.62** 

SURFACE EFFECT ON LIQUID CRYSTALS: A MICROSCOPIC STUDY, M.P.Valignat, D. Duca, R. Barberi, E. Dubois-Violette, A. M. Cazabat, R. Bartolino, Collège de France, Paris and INFM Research Unit of Cosenza, Italy.

We present an ellipsometric study of the spreading of mesogenic compounds on a solid substrate at the microscopic scale: - on bare silicon substrate, the 5CB (nematic) droplet may exhibit a "smectic-like" behavior close to the solid surface (two or three steps of around 30Å spread out, depending on the relative humidity and on the temperature). The 8CB (smectic) wets the surface and a precursor film grows which radius R scales like the square root of time t:  $R \approx \sqrt{Dt}$ . The diffusion coefficient D decreases with temperature and vanishes several degrees below the melting temperature, i.e., the solid phase also spreads out through a precursor film. The effect is analyzed in terms of surface induced premelting. - on evaporated surfaces, the thickness profile of the 5CB drop shows two typical lengths belonging to the microscopic and to the mesoscopic scales (few tens and some hundred of Å). No intermediate thickness are observed during the spreading. A simple model involving long and short range interaction is used to interpret the results. 8CB has the same behavior as the one observed on bare substrate.

**B4P.63** 

PHOTO-INDUCED DYNAMIC PATTERNS IN TWO-DIMENSIONAL SMEC TIC-C LIKE LIQUID CRYSTALLINE LANGMUIR MONOLAYERS, <u>Yuka Tabe</u> and Hiroshi Yokoyama, Molecular Physics, Electrotechnical Laboratory, Tsukuba, 305, Japan.

Purely light-driven spatio-temporal pattern formation has been found to take place in a liquid-crystalline Langmuir monolayer consisting of an amphiphilic azobenzene derivative, undergoing the trans cis photoisomerizations. The Langmuir-monolayer is in a smectic-C-like liquid crystal phase[1] whose two-dimensional orientation is easily perturbed by slight conformation changes in the constituent molecules. On illumination with a linearly polarized light, a collective and global in-plane reorientation of the azobenzene chromophores is induced over an existing static stripe texture, which finally yields a polarization-dependent steady state orientational patterns. Prolonged photoexcitation generates sustained traveling and solitary waves, associated with variations in molecular tilt directions.

[1] Y. Tabe and H. Yokoyama, J. Phys. Soc. Jpn. **63**, 2472 (1994); Langmuir **11**, 699 (1995); Langmuir **11**, 4609 (1995).

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THEORETICAL ANALYSIS OF TEXTURES SmC ON THE BASIS OF  $C_8H_{17}$  - BENZYLIDENE -  $C_6H_{13}$  - OXYPYRIMIDINE ON THE TWO POLYIMIDES FILMS SURFACES, <u>V.N.Ryzhov</u>, K.I.Guriev, S.P.Kurchatkin, Saratov State Pedagogical Institute, Michurina, 92, Saratov, 410028, Russia.

We have investigated textures SmC on the basis of  $C_8H_{17}$  - benzylidene -  $C_6H_{13}$  - oxipyrimidine on the surface of two polyimides: I - poly - (4, 4' - oxybiphenylene) piromillitamide acid, and II - poly - 4, 4' - [2, 2' -bis - 4 (4' - aminophenoxy) phenylpropyl] - biphenyloxytetracarbonic acid. Polarized microscopic textures SmC on the above mentioned compounds I, II differ greatly: the texture of SmC on the polyimide I is of "Shevron" character, and the texture of SmC on the polyimide II is of "microfan" character. Calculations of the intermolecular interaction energies (IMIE) enable to determine the nature of texture difference. For this purpose the supposed structure of polyimides had been calculated before. Some geometrical digital data of polyimides have been taken from [1]. The method of calculation IMIE is described in [2, 3]. In calculations the molecule SmC was oriented over the molecular polyimide profile in different way, and dependence of full IMIE on translation and rotation movement was determined in reference to coordinate axises. It has been stated that planar structure is realized over the polyimide I, and as for the polyimide II, the declined structure with approximately 15° angle of SmC molecule is realized. The types of textures depending on the length of monomer are discussed in this work.

[1] Polyimide - class termostoikih polymerov. Ed. M. Bessonov, L., 1983. [2] V.N. Ryzhov and et al. J. Phys. Chem. v.61, 1949(1987). [3] V.N. Ryzhov and et al., 1990, paper presented at the 13th ILC, Vancouver, Canada, 22-27 July.

C1P.02

ANOMALOUS THICKNESS DEPENDENCE OF TRANSITION TEMPERATURES A-C\*,C\*-C<sub>ferri</sub>, C<sub>ferri</sub> - C<sub>anti</sub> IN FREE STANDING FILMS, <u>E.I. DEMIKHOV</u>, Inst. of Solid State Physics, Acad. of Sciences, 142432 Chernoglovka, Russia; Univ. of Paderborn, Inst. Phys. Chem., 33095 Paderborn, Germany

The phenomenon of surface reconstruction of surface freezing type is well-known in liquid-crystalline systems. This means that the boundary regions possess some more ordered structure with respect to the films interior. If we neglect effects of the divergence of the order parameter fluctuations in 2D systems described in Landau-Paierls theorem, the surface ordering of such a kind causes the increase of the transition temperature with decreasing the number of layers. In ferroelectric films, the boundary layers can be less ordered with respect to the films interior. This effect results from taking into account the electrostatic interaction of the dipoles with depolarizing fields [1]. In this case the phase transition to the ferroelectric phase should be shifted to lower temperatures on decreasing the film thickness. It is shown that the phase transitions SmA - SmC\*, SmC\* - SmC<sub>ferri</sub>, SmC<sub>ferri</sub> -SmC<sub>anti</sub> of compound 14P1M7 are shifted to lower temperatures on decreasing the film thickness [2]. The stripe state has been observed in SmC\*, SmC<sub>ferri</sub>, SmC<sub>anti</sub> phases in thick films. The textural transition (change of the basic films texture) stripe state - schlieren occur in ferro-, ferri- and antiferroelectric phases by decreasing the number of layers. The features of this transition are discussed using the structural models of SmC\*, SmC<sub>ferri</sub>, SmC<sub>anti</sub> phases and the model of the stripe state [3]. [1]. R.Kretschmer et al., Phys.Rev B20, 1065 (1979); [2]E.I. Demikhov, JETP Lett. 61, 977 (1996); [3] E.I. Demikhov and S.A. Pikin et al., Phys. Rev. E 51, 5954 (1995).

C1P.03

EQUATION OF STATE AND DEVIL'S STAIRCASES IN ANTIFERROELECTRIC LIQUID CRYSTALS, \* X. Y. Wang and <u>P. L. Taylor</u>, Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079

The director configuration adopted by an antiferroelectric liquid crystal is a function of many variables, including the strength of the applied electric field and the location and nature of the surfaces with which the liquid crystal is in contact. We have developed an expression [1] for the energy of a cell containing an antiferroelectric smectic liquid crystal with only nearest-neighbor interactions between layers. From it we conclude that a critical cell thickness exists at which the commensurability of the system changes from unity to higher values, and that for negative dielectric anisotropy there is another critical thickness below which a transition to ferroelectric alignment cannot be homogeneously nucleated at any field. The transition to and from ferroelectric alignment propagates as a stable solitary wave under certain conditions at a speed which can be predicted from the model.

[1] X.Y.Wang and P.L.Taylor, Phys. Rev. Lett. 76, 640 (1996).

<sup>\*</sup> Work supported by the NSF ALCOM S & T Center under Grant DMR89-20147.



ANALYSIS OF ORIENTATION IN FERROELECTRIC LIQUID CRYSTALS BY POLARIZED FT-IR, J. Matsushima, K. Miyachi, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, and K. Takahashi\*, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan, \*NTT Interdisciplinary Research Laboratories, Musashino-shi, Tokyo 180, Japan

We have observed hindered rotation of C=O in a homogeneously aligned cell in SmC\* of NTT-FLC2 by polarized FT-IR. Since this compound contains keto, ester, and lactic acid groups, three C=O stretching peaks are observed. They show different dependencies on the polarization rotation angle, indicating that three C=O stretching direction have different hindered directions with respect to the molecular long axis. By comparing the obtained data with the simulated results following the Miyachi et al. 's procedure [1], we have determined the degree of hindrance and the hindered direction.

с, н, остно-с, н

[1]K.Miyachi et al. 's, Phys. Rev. E <u>52</u>, R2153 (1995).

C1P.05

CIRCULAR DICHROISM IN ANTIFERROELECTRIC LIQUID CRYSTALS. K. Yamada, K. Miyachi, Y. Takanishi, K. Ishikawa, H. Takezoe and A. Fukuda, Dept. of Org. and Polym. Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

We investigated Circular Dichroism (CD) in the mixture of (R)-MHPBC# and (S)-TFMHPBC##. In the SmCA\* phase, two induced CD peaks with shoulders were observed derived from helical structure. This result cannot be explained simply by considering two transitions of phenyl ring reported by Li et al.[1]. In the absorption spectroscopic measurement, a broad absorption band appears in the longer wavelength region of the absorption band due to the transitions of phenyl ring. In the SmC<sub>0</sub>\* phase we report the dependence of CD spectra on the sample thickness and mixing ratio. From the viewpoint of helicoidal structure, we consider whether the  $SmC_{\alpha}$ \* phase inherently has a helicoidal structure or not.

[1] J. Li. H. Takezoe, A. Fukuda and J. Watanabe, Liq. Cryst., 18, 239 (1995)

C1P.06

STRUCTURES WITH DOUBLE MODULATION IN ANTIFERROELECTRIC LIQUID CRYSTALS V.L. Lorman, Laboratoire de Physique de la Matière Condensée, Université de Picardie, Amiens, France

The analysis of possible inhomogeneous structures which can exist in the antiferroelectric liquid crystals (AFLC) is presented. It is shown that in the close vicinity of the paraelectric SmA phase there exists the phase with double modulation: both tilt and azimuthal angles, which is more stable than usual helicoidal ferroelectric (or antiferroelectric) phase. The decreasing of temperature transforms such a structure into ferroelectric one by way of phase transition. The structural difference disappears rapidly in an external electric field. The molecular organization, dielectric and optical properties of the proposed structure are compared with those of the SmCa phase in the tolan series of AFLC [1,2]. The temperature dependence of the pitch together with its apparent small value is discussed. The relation between the electroclinic effect (and the softness of the tilt mode) and the stability of the SmCa phase is demonstrated.

[1] Gisse P., Pavel J., Nguyen H.T., Lorman V, Ferroelectrics, 147, 27 (1993)

[2] P.Cluzeau, H.T.Nguyen, C.Destrade, N.Isaert, P.Barois, A.Babeau, Mol. Cryst. Liq. Cryst. 260, 69 (1995)

INTERLAYER INTERACTIONS IN ANTIFERROELECTRIC LIQUID CRYSTALS, M. Čepič<sup>+\*</sup> and B. Žekš<sup>+</sup>, <sup>+</sup>J.Stefan Inst., Jamova 39, \*Faculty of Education, Kardeljeva pl.16, 1111 Ljubljana, Slovenia. Paying regard to discrete smectic layer structure of antiferroelectric liquid crystals and assuming the existence of interlayer interactions up to the next nearest layers, the Landau expansion of the free energy has been proposed, that predicts the existence and the structure of Sm  $C^*_{\alpha}$  phase [1]. Including some higher order terms in the tilt order parameter, the predicted structures and properties of phases as well as the sequences of phases in these systems are consistent with experimental observations [2].

The discrete model assumes the existence of the interlayer interactions, that are shown to be of steric, dipolar and quadrupolar microscopic origin. The steric interactions prefer parallel alignment of the molecules in nearest as well as in next nearest layers, while dipolar interactions favour antiparallel alignment. The quadrupolar interactions have shorter range and leads to perpendicular tilt directions in nearest layers. The competition between steric, dipolar and quadrupolar interactions results in appearance of different phases at different temperatures. A consistent theoretical explanation of different observed miscibility phase diagrams [2] will also be given.

[1] M.Čepič, B. Žekš, Mol. Cryst. Liq. Cryst., 263, 61 (1995).

[2] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, J.Mater. Chem., 4, 997 (1994).

C1P.08

OPTIC-LIKE PHASE MODE IN ANTIFERROELECTRIC LIQUID CRYSTAL, I. Musevic, A.Rastegar, M. Cepic, B. Zeks, M. Copic, J. Stefan Institute and Dept. of Physics, University of Ljubljana, Slovenia, and G. Heppke, Iwan N.Stranski Institut, T. U. Berlin, Germany

In a quasielastic light scattering experiment we have observed an acoustic-like and an optic-like branch of phase excitations in the antiferroelectric SmC\*\*\_A liquid crystal phase. The acoustic branch represents the antiferroelectric symmetry restoring mode with zero relaxation rate at the wave vector of the helix. The optic branch is a ferroelectric-type phase mode which always has a finite relaxation rate. The phenomenon is a direct consequence of the doubling of smectic unit cell at the transition from the SmA phase. We obtain a remarkable agreement with a Landau-de Gennes type model. Among several other parameters we determine for the first time the coupling coefficient between the ferroelectric and antiferroelectric ordering.

C1P.09

SIMULTANEOUS OBSERVATION OF ELECTRIC FIELD COUPLING TO LONGITUDINAL AND TRANSVERS FERROELECTRICITY IN A LIQUID CRYSTAL, Darren R. Link, Joseph E. Maclennan, Noel A. Clark, Department of Physics, University of Colorado, Boulder, CO, 80309, USA.

We report novel odd-even layering effects in freely suspended films of the chiral liquid crystal MHPOBC in its antiferroelectric smectic phase. Films with an odd number of smectic layers are characterized by transverse ferroelectricity (molecular tilt plane perpendicular to applied electric field E) while films with an even number of layers exhibit longitudinal ferroelectricity (molecular tilt plane parallel to E). This is the first observation of the simultaneous electric field manipulation of longitudinal and transverse ferroelectric polarization in liquid crystals.



<sup>\*</sup> Supported by NASA GRANT NAG3-1600 and NSF GRANT DMR-92-23729



SC\*A, SC\* AND TGBA PHASES IN CHIRAL NON SYMMETRIC DIMESOGENS.,

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V. Laux, N. Isaert, Université de Lille 1, 59655 Villeneuve d'Ascq, France.

We have synthesized three separate homologous series of chiral non-symmetric dimesogens: a polar series which exhibits a TGBA phase and a two phenyl rings moiety bearing a terminal alkoxy chain is related to a chiral three phenyl ring mesogen displaying itself antiferroelectric properties, via a methylenic spacer. Depending on the parity of the number of carbons constituting the spacer, two kinds of mesomorphic behaviour have been found. When the spacer is even, various  $S_{C}$ \* phases  $(S_{C}$ \*A,  $S_{C}$ \*FI,  $S_{C}$ \*,  $S_{C}$ \* $\alpha$ 0 have been undoubtly identified, whereas when the spacer is odd, a tilted modulated phase  $(S_{C}$ \*) has been observed and characterized. In each case, we study the effect of the alkoxy chain length at the end of the short moiety.

## C1P.11

PHYSICAL PROPERTIES OF LIQUID CRYSTALS EXHIBITING ANTIFERROELECTRIC CHIRAL SMECTIC I PHASES

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Materials exhibiting the antiferroelectric SmC (SmC\*<sub>A</sub>) phase are well known and the driving force behind the formation of this phase is thought to be the pairing of the transverse dipole moments of the molecules in neighbouring layers. Other antiferroelectric smectic phases exist, and in particular one that usually occurs as a monotropic phase has been tentatively designated as the antiferroelectric SmI\* phase (SmI\*<sub>A</sub>). To date there have been very few reports of the SmI\*<sub>A</sub> phase, possibly because the increased layer spacing hinders pair formation. However, the phase exhibits interesting properties and miscibility studies raise questions about its symmetry that are investigated further here. Current pulse and optical hysteresis measurements are presented for several new materials and their mixtures exhibiting SmI\*<sub>A</sub> phases. One of the materials has a ferroelectric SmI\* phase below the SmI\*<sub>A</sub> phase. Additional electro-optic measurements and miscibility studies further elucidate their phase behaviour, symmetry and switching characteristics.

#### C1P.12

LONG RANGE INTERACTIONS, MANY BODY FORCE AND MESOPHASES IN FERRO-ELECTRIC SMECTICS\*, M.Yamashita, Tokushima College of Technology, Itano, Tokushima 779-01, JAPAN

By using the ANNNI model with the third nearest neighbour interaction J3, we have explained the successive phase transitions in ferroelectric smectics and sugested the structure of mesophases FIL and FIH appearing there [1]. We also predict mesophases between SmC\* and AF on the basis of this model, which is observed latter [2]. As to the negativeness of the second nearest neighbour interaction parameter J2 in addition to the assumption of J3, we have found the physical ground in introducing the head-tail freedom of the molecular long axis [3]. In this theory we also found the many body forces. Here, the structure of the mesophase between SmC\* and AF and the effect of the four body force which twins J3 with are studied.

[1] M. Yamashita and S. Miyazima, Ferroelectrics 148, 1(1993). M. Yamashita, Mol. Cryst. Liq. Cryst. 263, 93(1995); to appear in Ferroelectrics (1996). [2] J. Hatano et al., Jpn. J. Appl. Phys. 33, 5498(1994). [3] M. Yamashita, preprint submitted to J. Pyhs. Soc. Jpn.

\*Supported partly by a Grant-in-Aid for Scientific Research on Priority Areas "Cooperative Phenomena in Complex Liquids" from the Ministry of Education, Science and Culture.

FREEDERICKSZ-EFFECT AND BOND-ORIENTATIONAL ORDER IN SMECTIC LIQUID CRYSTALS WITH TILTED MOLECULES, <u>Peter Schiller</u>, Karifa Camara and Gerd Pelzl, Institut für Physikalische Chemie, Mühlpforte 1, 06108 Halle/Saale, Germany

In the smectic phases I and F the molecules are tilted towards the layer plane. Although the crystalline lattice is molten, a bond orientational order still exists. This order results from the alignment of the lines (bonds) connecting the centres of gravity of neighbouring molecules. If elastic distortions occur, both the tilt direction defined by a director and the bond directions should deviate from their initial alignment. The continuum theory was used to investigate the Freedericksz-transition of a hexatic phase with tilted molecules [1]. In accordance with the experimental results the threshold voltage was found to be strongly dependent on the the film thickness. This dependence results from the coupling between the director and the bond net. We have estimated several elastic constants and the coupling constant by fitting the formula for the threshold voltage to experimental data.

[1] P. Schiller, G. Pelzl and K. Camara, Liquid Crystals, 19, 113 (1995)

C1P.14

MIXING-INDUCED ANTIFERROELECTRIC STRUCTURE IN BINARY SMECTIC C LIQUID CRYSTAL SYSTEMS, Y. Ouchi, T. Toyoda, Y. Yoshioka, H. Ishii, K. Seki, M. Kitamura, R. Noyori, Y. Takanishi<sup>1</sup> and I. Nishiyama<sup>2</sup>; Department of Chemistry, Nagoya University, Nagoya 464, Japan, <sup>1</sup>Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152, Japan, <sup>2</sup>Toho Titanium Co. Ltd., Kanagawa 253, Japan

Though much synthetic effort has been devoted, the antiferroelectric smectic C (SmC<sub>A</sub>) phase<sup>1)</sup> has been observed in a limited molecular-structural group or in their mixtures. In the present study, we have found for the first time that the SmC<sub>A</sub> phase has been induced in a binary mixture of smectic C (SmC) compounds. Binary mixtures investigated are 1PenPOBC (4-(1-Pentylheptyloxy carbonyl)phenyl 4'-Octyloxybiphenyl-4-carboxylate) and 8OSI (4-(2-Methylbutyl)phenyl 4'-Octyloxybiphenyl-4-carboxylate). The SmC<sub>A</sub> phase has been confirmed by polarizing-microscope observation and X-ray study. Chirality effect on the appearance of the induced SmC<sub>A</sub> phase will be discussed.

[1] A.D.L. Chandani et al., Jpn. J. Appl. Phys., 28(1989)L1265.

C1P.15

PYROELECTRIC PROPERTIES OF ANTI-FERROELECTRIC LIQUID CRYSTALS, J. W. O' Sullivan, Yu. P. Panarin, J. K. Vij, Department of Electronic and Electrical Engineering, University of Dublin, Trinity College, Dublin 2, Ireland. A. J. Seed, M. Hird and J. W. Goodby, School of Chemistry, University of Hull, Cottingham Road, Hull, HU6 7RX, U. K.

The pyroelectric properties of a antiferroelectric liquid crystal are investigated. The pyroelectric results are interpreted with the aid of spontaneous polarization measurements made as functions of temperature and applied voltage. These are shown to exhibit the temperature and field induced "Devil's Staircases". We find that for SmA-SmC\*-AF-SmC\* $\gamma$  phase transitions, the pyroelectric and polarization measurements do agree qualitatively. However for the SmC\* $\gamma$ -SmCA phase transition, the pyroelectric measurements do not agree with the spontaneous polarization measurements. In the antiferroelectric and ferrielectric phases the integrated pyroelectric signal does not follow the temperature dependence of spontaneous polarization. The main reason for this disagreement are the large relaxation times of the antiferro-ferrielectric phases. The unusual behaviour within the SmC\* region could be explained by the existence of a field induced ferrielectric metastable state with qE = 4/5.



ELECTRO-OPTIC EFFECT IN AN ANTIFERRO-ELECTRIC LIQUID CRYSTAL,

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In antiferroelectric liquid crystals, it has been found by Hiraoka  $et\ al.$  that the antiferroelectric Goldstone mode can be excited by an electric field in  $SmC_A^*$ , though it responds to the square of the field, but not to the field itself. In their experiment, however, homogeneous cells were used and so expected behaviors such as the divergence of the relaxation time were not observed due to the anchoring of molecules on the glass surfaces. In this paper we have measured the electro-optic effect in free-standing films, which are free from the surface anchoring. We discuss the result on the basis of our theory in which the transmitted intensity in the electro-optic measurement was derived from a phenomenological equation of motion.[1]

[1] H. Orihara and Y. Ishibashi, J. Phys. Soc. Jpn. 64, 3775 (1995).

## C1P.17

THE SYNTHESIS AND CHARACTERISATION OF A NOVEL THIOPHENE-BASED LIQUID CRYSTAL EXHIBITING FERRO-, FERRI- AND ANTIFERROELECTRIC PHASE TYPES, David J. Byron\*, Lachezar Komitov\*\*, <u>Avtar S. Matharu</u>\*, Ian McSherry\*, and Robert C. Wilson\*. \*Department of Chemistry and Physics, The Nottingham trent University, Clifton Lane, Nottingham, NG11 8NS. \*\*Department of Physics, Chalmers University of Technology, S-412 96 Goteborg, Sweden.

The synthesis and liquid crystal properties of R-(-)-4-(1-methylheptyloxycarbonyl)phenyl 5-(4-n-decyloxyphenyl)-thiophene-2-carboxylate is reported. This novel material exhibits the  $S_c$ \*ferro-, ferri- and antiferroelectric phase types which have been characterised primarily by thermal optical microscopy, miscibility and differential scanning calorimetry coupled with further evidence from electro-optical studies.

#### C1P.18

# ELECTROOPTIC ANOMALIES IN ANTIFERROELECTRIC LIQUID

CRYSTALS\*; Elizabeth E. Shack, <u>Jian-feng Li</u>, Xin-Yi Wang, Hua Zhong, Rolfe Petschek, and Charles Rosenblatt, Physics Dept., Case Western Reserve Univ., Cleveland, Ohio 44106 USA; <u>Mary E. Neubert</u>, Liquid Crystal Inst., Kent State Univ., Kent, Ohio 44242 USA; and <u>Yoshi-ichi Suzuki</u>, Showa Shell Sekiyu Kabushiki Kaishi, Kanagawa-ken, Japan

Several interesting electrooptic phenomena have been observed in antiferroelectric liquid crystals and their subphases. In the Sm  $C_{\gamma}^*$  phase of MHPOBC we found a nonmonotonic variation of the effective polar tilt angle  $\theta_{eff}$  with electric field: In a certain high field range a peak was observed in  $\theta_{eff}$ , beyond which  $\theta_{eff}$  falls and then levels off at some lower value. In addition, above the Sm A - Sm  $C_A^*$  transition in right- and left-handed mixtures of TFMHPOBC we have observed and measured the nonlinear part of the tilt susceptibility,  $d\theta_{eff}$  / dE, as a function of concentration. The results have been modeled in terms of a mean field theory.

\* Supported by the NSF under grant DMR-9502825 and by the NSF's Advanced Liquid Crystalline Optical Materials Science and Technology Center under grant DMR-8920147

THE MOLECULAR ORIGIN OF THE MULTIPLE ABSORPTION PEAKS IN THE DIELECTRIC SPECTRUM OF THE FERRIELECTRIC AND ANTIFERROELECTRIC LIQUID CRYSTALS.

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In the dielectric spectrum (1 Hz-10 GHz) of ferrielectric and antiferroelectric smectic C\* phases four absorption peaks are observed in a measurement geometry where the smectic layers are essentially perpendicular to the cell plates. When the smectic layers were aligned in a direction parallel to the cell plates, the dielectric spectrum contains, in most cases, one absorption peak which is connected with the molecular reorientation around the short axis. In the low frequency region (10 Hz to 10 MHz) the dielectric spectrum, of the compounds which do not posses a C\* phase, exhibits only two absorption peaks. However, the spectrum of the ferrielectric  $C_{\gamma}^*$  and the antiferroelectric  $C_{A}^*$ , if preceded by a ferroelectric C\* phase, shows three absorption peaks. The additional process may be attributed to a coexistence of the C\* phase with the  $C_{\gamma}^*$  and  $C_{A}^*$  phases, due to the first order nature of the C\* -  $C_{\gamma}^*$  -  $C_{A}^*$  phase transitions. Measurements on four compounds are taken together to attribute these peaks to specific collective and molecular motions.

C1P.20

INFLUENCE OF STRUCTURE OF DOPANTS ON THEIR ABILITY TO ENHANCE S<sub>C</sub> PHASE <u>W.Drzewiński</u>, R.Dąbrowski, Z.Raszewski, J.Rutkowska, Military University of Technology, 01-489 Warsaw, Poland M.Neubert, Institute of Liquid Crystals, Kent, Ohio, USA

Six two ring chiral esters of formula 1 and 2 being isotropic liquids were tested as dopants inducing ferroelectricity in non-chiral S<sub>C</sub> mixtures composed from esters [1] or pyrimidines and esters.

$$H_{13}C_6 - \overset{\circ}{C}H_{-0} - \overset{\circ}{C}C_{-0} -$$

 $Y = OC_nH_{2n+1}$  (a),  $OCOC_nH_{2n+1}$  (b),  $COC_nH_{2n+1}$  (c)

The chiral dopants 1a, b, c and 2a depress the smectic C phase stability. Compound 2b and specially 2c strongly enhance the stability of smectic C phase up to the concentration of 30 wt.%. The dependence of spontaneous polarization, tilt angle, dielectric parameters of GM mode upon the concentration of compound 2c was tested. Compounds 2a is found as promising chiral dopant for the preparation of ferroelectric mixtures.

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C1P.21

#### GEOMETRICAL AVERAGING OF AFLC DIELECTRIC TENSORS.

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For the calculation of the optical transmission through AFLC's, anisotropic diffraction grating theory should be applied. For normal visible light the conclusion is fairly simply: one should average the periodical dielectric tensor. In this article we make the geometrical study of this averaging. Without the numerical calculation, we want to predict how the new principal axes of birefringence are oriented, and what the values of the new main indices are. Especially in non-symmetrical molecular positions (e.g. during the switching process) this averaging is not trivial. Representing dielectric tensors by ellipsoids, one can ask for the ellipsoid that corresponds with the averaged tensor. Illustrative figures demonstrate the different cases that may occur.



PHASE DIAGRAMS OF ANTIFERROELECTRIC LIQUID CRYSTALS IN FILMS, <u>Barbara</u> Rovšek, Mojca Čepič and Boštjan Žekš, J. Stefan Institute, Jamova 39, 1111 Ljubljana, Slovenia.

Phase diagrams of antiferroelectric liquid crystals in films with finite number of smectic layers are studied theoretically within a discrete phenomenological model assuming the existence of competing nearest- and next-nearest-layers interactions [1]. Excluding chirality effects, by lowering the temperature the transition from the SmA phase is always to a planar phase, characterized by the in-plane tilt of the director everywhere in the film. The structure of the planar phase depends on the model parameters and could be ferroelectric or antiferroelectric as the two extrema. By further cooling the planar phase suffers the transition to the SmC $_{\alpha}$  phase with structure proposed in [1]. Enough below the SmA phase the constant amplitude approximation is valid and we use it to study the structure and optical properties of the film. For large number of layers the structure of the SmC $_{\alpha}$  phase in the film is similar to the bulk SmC $_{\alpha}$  phase. Discrepancies are limited to the free surfaces of the film and are due to the fact that the surface layers have the neighboring layers, which they interact with, just on one side. We calculate the average dielectric tensor, which determines the refraction of light in the film, for different structures appearing in the phase diagram. We find our results in fair agreement with the experimental data obtained by ellipsometry for free standing films [2].

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## C1P.23

STRUCTURE ANALYSIS OF THE ANTIFERROELECTRIC HEXATIC SmI<sub>A</sub>\* PHASE BY X-RAY DIFFRACTION AND NMR SPECTROSCOPY,

Y. Takanishi, T. Mitsumori, S. Yoshida, K. Ishiakwa, H. Takezoe and A. Fukuda, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

We have studied the layer structure and molecular orientation in the antiferroelectric hexatic  $\mathrm{SmI}_A^*$  phase in (R)-4-(1-trifluoromethylheptyloxycarbonyl)phenyl 4'-nonylcarbonyloxy biphenyl-4-carboxylate (TFMHPNCBC). By X-ray measurement, higher-order Bragg peaks up to the fifth order corresponding to the layer spacing were observed, and we found that the third order peak becomes larger than the second order peak at the phase transition from  $\mathrm{SmC}_A^*$  to  $\mathrm{SmI}_A^*$ , indicating the different density distribution between two phases. We have also investigated whether this change is caused by the conformational change or the change of molecular orientation in a layer at the transition by NMR spectroscopy, and discussed the difference of the stability and the origin of its appearance in two phases.

## C1P.24

STUDY OF MOLECULAR STRUCTURE AND ORIENTATION IN ANTIFERRO-ELECTRIC LIQUID CRYSTALS BY NMR SPECTROSCOPY, S. Yoshida, B. Jin, Y. Takanishi, K. Ishikawa, H. Takezoe and A. Fukuda, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan.

Temperature dependence of <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra have been measured in the SmA, SmC(\*) and SmC<sub>A</sub>(\*) phases in MHPOBC and TFMHPOBC. From the <sup>13</sup>C NMR spectra without sample spinning, we have confirmed that the layer normal is parallel to the high magnetic field. Besides we have found that the temperature dependence of orientational order of the carboxyl group near the chiral center is different from that of the other carbons' in the core part of MHPOBC. The results of <sup>13</sup>C NMR with CP/MAS experiments have indicated the conformational changes in the core part of MHPOBC at phase transitions from SmA to SmC(\*) and from SmC(\*) to SmC<sub>A</sub>(\*). We have observed that the orientational order parameter of -CF<sub>3</sub> group in racemic TFMHPOBC jumps at the phase transition from SmC to SmC<sub>A</sub> by means of <sup>19</sup>F NMR. It is considered that this jump is caused by the conformational change at the chiral part. We conclude that the confomational changes near the chiral part is important at the phase transitions in the antiferroelectric liquid crystals.

MODULATED PHASE IN ANTIFERROELECTRIC LIQUID CRYSTALS\*, <u>Hua Zhong</u>, Erik Kangas, and Rolfe G. Petschek, Physics Department, Case Western Reserve University, Cleveland, OH, 44106-7079, USA.

We study the phase diagrams of smectic antiferroelectric liquid crystals using the phenomenological Landau theory, where the interactions between the electric polarization in neighboring layers are explicitly taken into account. We also consider the most general functional forms of the ferroelectric and antiferroelectric order parameters, *i.e.* they are no longer restricted to a simple helicoidal structure. Minimizing the free energy, we find that in most of the temperature range the system prefers to be in an unmodulated ferroelectric, antiferroelectric or ferrielectric phase. However, close to the critical point in the phase diagram, it is energetically favorable for the system to be in a modulated phase where the phase difference between the ferroelectric and antiferroelectric order parameters varies in space.

\* Supported by ALCOM and the Ohio Boards of Regents.

C1P.26

INVESTIGATIONS ON A HELIX-COMPENSATED ANTIFERROELECTRIC LIQUID CRYSTALLINE MIXTURE, G. Heppke, D. Lötzsch, <u>D. Moro</u> and S. Paus, Iwan N. Stranski Institute, Technische Universität Berlin, Sekr. ER 11, Straße des 17. Juni 135, D-10623 Berlin

The observable dielectric properties of the ferroelectric SmC\*-phase (Goldstone mode, soft mode) are well understood in the framework of the dynamic properties of the phase structure. On the contrary, for the antiferroelectric SmC\*-phase [1] the molecular motions related to the detectable modes by dielectric spectroscopy are in spite of numerous investigations still not clear and are discussed controversially in literature (see i.e [2,3]).

In order to clarify this situation we investigated a helix-compensated mixture of (S)-EHPOCBC and (S)-TFMHPOBC with a non-vanishing polarization due to the inverse dipole moment of the trifluoromethylgroup of TFMHPOBC at the chiral center with respect to the first compound. Methods used include dielectric spectroscopy, electro-optical measurements, DSC measurements and optical relaxation spectroscopy.

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C1P.27

DIASTEREOMER EFFECT ON ANTIFERROELECTRICITY AND FERROELECTRICITY OF THE LIQUID CRYSTALS, <u>Ichiro kobayashi</u>, Yoshiichi Suzuki, Tomoko Yajima\*, Masahiro Terada\*, and Koichi Mikami\*, Showa Shell Sekiyu K.K., Central Research Laboratory, Shimokawairi 123-1, Atsugi-shi, Kanagawa 243-02, Japan\*, Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

We have reported that the chiral titanium complex-catalyzed carbonyl-ene reaction with fluoral serves as an efficient route to the diastereoselective and enantioselective synthesis of CF3-substituted compounds.[1] Herein disclosed is the antiferroelectric and ferroelectric liquid crystals of the chiral portion synthesis by on the bases of fluoral-ene reaction.

Antiferroelectricity and ferroelectricity of the liquid crystals in terms of the thermal stability are concluded to depend on the stereochemical purity of the diastereomeric chiral portion.

[1] K. Mikami et.al. Tetrahedron, 1996, 52, 85



TEMPERATURE DEPENDENCE OF ANTIFERROELECTRIC LIQUID CRYSTAL DEVICE'S CHARACTERISTICS, Weisong Zhao, Ruipeng Sun, Ximin Huang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, P.R.China

Antiferroelectric liquid crystal ( AFLC) display's cone angle \ responding time \ contrast ratio electric-optical characteristics was investigated at variable temperature. The result of the experiment shows that the temperature's variation has large effect on the characteristics of the AFLC's panels. Then we discussed the distortion of AFLC divice's gray scale level and contrast ratio that caused by the variation of temperature. Then we proposed the method to solve this problem.

[ 1 ] J. MATER. CHEM., 4 , (1994)

## C1P.29

SIMULATION OF SWITCHING IN ANTIFERROELECTRIC LIQUID CRYSTALS, J. Fornier, E. De Ley, B. Verweire and A. De Meyere, Department of Electronics and Information Systems, University of Gent, Sint-Pietersnieuwstraat 41, B-9000 Gent, Belgium.

We are simulating the dynamic response of surface stabilised antiferroelectric liquid crystal displays, based on a one-dimensional approach. For the first time, we are using a justified elastic energy. This leads to more detailed modelling, than before [1]. The evolution of director profiles and the resulting optical transmission under applied voltages are studied. The different switching modes between the alternating state and the two uniform states, observed in antiferroelectric test cells, can be understood fairly well. The model incorporates a chevron geometry. The different terms in the bulk energy function can be rationally interpreted. The alignment layers are modelled by a polar and a non-polar surface energy term. The influence of parameters, such as the antiferroelectric coupling parameter, the polar and non polar anchoring strength, the elastic constants etc. are discussed.

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#### C1P.30

EFFECT OF THE EXTERNAL TWIST ON MOLECULAR SWITCHING IN ANTIFER-ROELECTRIC LIQUID CRYSTALS, <u>Jae-Hoon Kim</u>, Ju-Hyun Lee, Jong Bong Lee, and Sin-Doo Lee\*, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

We have studied the molecular switching and the electro-optic (EO) effect in twisted antiferroelectric liquid crystals (AFLCs). In contrast to a planar structure of AFLCs, the twisted one exhibits better threshold characteristics and gray scale capability. In a twisted geometry, the smectic layers are formed perpendicular to the cell surface such that the molecular director experiences twist by twice of the molecular tilt on going from one substrate to the other. In a model with dipolar interactions between the nearest neighboring layers, the director profiles of two adjacent layers and the resultant EO modulation were obtained as a function of an external electric field.

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<sup>\*</sup>Supported in part by RCDAMP through Pusan National University.

THRESHOLDLESS SWITCHING IN HOMOGENEOUS CELLS AND ANTIFERROELECTRIC CONOSCOPIC FIGURES IN HOMEOTROPIC CELLS AS OBSERVED IN A BINARY SM-C\*-LIKE MIXTURE, S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, C. Tanaka<sup>†</sup>, T. Fujiyama<sup>†</sup>, T. Maruyama<sup>†</sup>, and S. Nishiyama<sup>†</sup>, Tokyo Institute of Technology, Tokyo 152, Japan and <sup>†</sup>Mitsui Petrochemical Industries, Ltd., Chemical Synthesis Laboratories, Chiba 299-02, Japan

Ordinary antiferroelectric liquid crystals (AFLCs) are characterized by tristable switching with DC threshold and hysteresis. Recently, however, some apparently AFLC mixtures were reported to show thresholdless V-shaped switching, which is usable for realizing attractive displays characterized by extremely wide viewing angle with very large contrast ratio, high speed response, and ideal analog gray scale with no hysteresis. To elucidate the origin of the extraordinary switching, we observed the electric field induced changes of conoscopic figures in free-standing films of a binary mixture which shows the V-shaped switching in homogeneously aligned cells [1]. The phase sequence observed in the free-standing film is Iso(100°C)Sm-A(79°C)Sm-C\*(59°C)FI(56°C)AF(34°C)ferri(32°C) ferro-Cry. Preliminary X-ray studies indicate that the ferroelectric phase appears to be Sm-I\* but not Sm-C\*. Consequently, the sequence is quite ordinary. AF exists in the wide temperature range and its helical pitch is too long (>2.5 µm) to be measured by a conventional spectrophotometer. These results suggest that not only the frustration between ferro- and antiferro-electricity but also some interface effects play an important role in the emergence of V-shaped switching.

[1] C. Tanaka et al., Abst. of 21th Jpn. LC Conf. (Sendai, 1995) 2C18.

C1P.32

SMECTIC LAYER ROTATION IN ANTIFERROELECTRIC LIQUID CRYSTAL CELLS WITH RUBBED ALIGNMENT POLYMER, T. Fujikawa, N. Yamamoto and Y. Yamada, Research Laboratories, Nippondenso Co., Ltd., 500-1, Minamiyama, Komenoki-cho; Nisshin-shi, Aichi 470-01, Japan

Antiferroelectric liquid crystal (AFLC) is one of the most promising materials to realize a display with high contrast ratio, wide viewing angle and fast response [1]. Smectic layer rotation in the AFLC cells without surface treatment for a unidirectional alignment has been reported [2]. From practical point of view, this phenomenon makes worse the quality of AFLC device. We paid attention to the anchoring of alignment polymer film, and studied the smectic layer rotation in AFLC cells with rubbed alignment polymer. According to the microscopic observation upon application of electric field, we found that the layer rotation angle was in proportion to the difference between  $\tau_d^+$  and  $\tau_d^-$  indicate the response time from the positive ferroelectric (F) state to the antiferroelectric (AF) state and that from the negative F state to the AF state, respectively. The difference between  $\tau_d^+$  and  $\tau_d^-$  was caused by that of rubbing strength between two substrates.

[1] N. Yamamoto, N. Koshoubu, K. Mori, K. Nakamura and Y. Yamada, Ferroelectrics, 149 (1993) 295. [2] M. Ozaki, H. Moritake, K. Nakayama and K. Yoshino, Jpn. J. Appl. Phys. 33 (1994) L1620.

C1P.33

MECHANISM OF GRAYSCALE GENERATION IN ANTIFERROELECTRIC LIQUID CRYSTAL DISPLAYS, J. Sabater, C. Rodrigo, X. Quintana, and J.M.Otón, Departamento de Tecnología Fotónica, ETSI Telecomunicación, Ciudad Universitaria, E-28040 Madrid Spain

Multiplex-compatible, analog grayscale has been recently demonstrated in antiferroelectric liquid crystal cells [1]. The grayscale generation mechanism, however, is not fully understood yet. Average transmission of multiple microdomains having slightly different switching properties has been proposed as the most plausible explanation [cita o autocita]. However, this explanation implicitly assumes that microdomains are independent to each other. Time resolved transmission of antiferroelectric cells has been used to test this hypothesis. Variations of the transmission with voltage and duration of the selection pulse, bias level, and temperature, have been related to possible relaxation mechanisms. The experimental conditions for which long-term evolution of the cell switched area depends on the bias voltage and/or on the selection pulse have been established as well.

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BROAD-BAND DIELECTRIC SPECTROSCOPY ON THE MOLECULAR DYNAMICS OF DISCOTIC CHOLESTERIC LIQUID CRYSTAL(DCLC) MIXTURES, <u>H. Xu</u>, F. Kremer, Faculty of Physics, Leipzig University, 04103 Leipzig, Germany. D. Kaueerke, M. Müller, G. Heppke, Technical University of Berlin, I.-N.-Stranski-Institute, D-10623 Berlin, Germany.

Broad-band dielectric spectroscopy  $(10^{-2}-10^9~\text{Hz})$  is employed to study the molecular dynamics in two CDLC mixtures where the helical axis is oriented either parallel or perpendicular to the electrodes. For frequencies below  $10^6~\text{Hz}$ , two relaxation processes are observed. In the frequencies between  $10^6-10^9~\text{Hz}$ , one molecular process exists which is assigned to the librational motion of the polar side groups ( $\beta$ -relaxation) in the CDLCs. The dielectric response of the  $\beta$ -relaxation in CDLCs is found to be affected by the different cell geometries. The observed dynamic processes are discussed in comparison with that in the columnar phase of a discotic ferroelectric liquid crystal[1-2].

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## C1P.35

FREDERIKS TRANSITION AND ELECTROCONVECTION IN SMECTIC C\* LIQUID CRYSTAL FILMS, S. Ried<sup>†</sup>, H. Pleiner<sup>‡</sup>, W. Zimmermann<sup>‡</sup>, and H.R. Brand<sup>‡</sup>, <sup>†</sup>Max-Planck-Institute for Polymer Research, Mainz, <sup>‡</sup>IFF, Forschungszentrum Jülich, <sup>†</sup>Theoretische Physik III, Universität Bayreuth, FRG.

The generalized Frederiks transition as well as electroconvection in freely suspended smectic C\* films are theoretically investigated. The additional ferroelectric torque (compared to nematic liquid crystals) leads to rather complicated bifurcation scenarios even in the case of DC Frederiks transitions. There are two different instability branches and a restabilization curve. Depending on material parameters these transitions switch from being continuous to discontinuous. If the polarization is large enough and antiparallel to the external field, a Frederiks transition is possible even for negative dielectric anisotropy. In a certain parameter range the restabilization of the homogeneous state is not obtained, since the latter exists as an isolated solution, only.

In the case of AC electroconvection a new subharmonic regime is found that emerges as a function of the external AC frequency between the dielectric and conductive one, if the polarization is large enough. Here all degrees of freedom oscillate at the onset with half the external frequency and the characteristic wavelength of the pattern is noticeably distinct from that of the other regimes. Reducing the polarization this regime vanishes via a codimension-3-point. It does not follow the usual Carr-Helfrich mechanism and allows electroconvection even for a vanishing or a slightly negative anisotropic part of the electric conductivity.

The competition between (DC) Frederiks transition and (DC) electroconvection is discussed in detail.

### C1P.36

INVESTIGATION OF RELAXATION PROCESSES IN AFLC USING WIDE RANGE DIELECTRIC SPECTROSCOPY. Yu.P.Panarin, O.E.Kalinovskaja, <u>I.K.Vij.</u> Dept. of EEE, Trinity College, Dublin, Ireland.

We investigated the dielectric properties of a Antiferroelectric Liquid Crystal (AFLC) over a wide range of frequencies ( $10^2$ - $10^9$  Hz). In this range the dielectric spectra exhibit two individual molecular  $\beta$ -relaxations (around the short and long axis) and two collective modes  $^1$ . The relaxation frequency and dielectric strength of  $\beta$ -relaxations depend only on the average molecular orientation with respect to applied electric field. The application of bias field at first decreases the dielectric strength of  $\beta$ -relaxation around long axis which corresponds to helix distortion due to dielectric anisotropy. Further increase of bias voltage induces the spontaneous polarization and hence increases the dielectric strength of the  $\beta$ -relaxation. The origin of relaxation processes in AFLC is discussed in terms of experimental results.

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HIGH FREQUENCY DIELECTRIC STUDY ON ANTIFERROELECTRIC LIQUID CRYSTALS M.R. de la Fuente, S. Merino, M.A. Pérez Jubindo, and B. Ros\*, Departamento de Física Aplicada II, F. Ciencias, Universidad del País Vasco, Apdo. 644, E48080 Bilbao, Spain. \*Departamento de Química Orgánica-Instituto de Ciencia de Materiales de Aragón, F. Ciencias, Universidad de Zaragoza-C.S.I.C, E50009 Zaragoza, Spain.

We report high frequency dielectric measurements in two compounds showing the antiferroelectric  $SmC_A^*$  phase. Compound I [1], with a biphenyl group in the core, shows the phase sequence I-SmA-SmC<sub> $\alpha$ </sub>\*-SmC<sub> $\gamma$ </sub>\*. We have analyzed the relaxation related to rotations around molecular long axis from the I phase to the  $SmC_A^*$  phase. This relaxation has a Havriliak-Negami shape but it is no so broad as it is in other ferroelectric liquid crystals. The frequency shows a jump (increase) at the I-SmA phase transition. Both facts would suggest that the molecules of our compounds are quite rigid.

[1] M.R. de la Fuente, S. Merino, Y. González, B. Ros, J.A. Puértolas, M. Castro, *Advanced Materials*, **7**, 564, 1995.

. C1P.38

NONLINEAR DIELECTRIC RELAXATION SPECTROSCOPY OF ANTIFERROELECTRIC LIQUID CRYSTALS, Y. Kimura and R. Hayakawa, Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, JAPAN.

The linear and third-order nonlinear dielectric spectra of the antiferroelectric liquid crystals have been experimentally studied in their Smectic A, Smectic C\* and Smectic C<sub>A</sub>\* phases. Both dielectric constants show a critical behavior in the SmA phase near the SmA-SmC\* or SmA-SmC<sub>A</sub>\* phase transition temperature corresponding to the softening of ferroelectric soft mode. The sign of the increment for the third-order nonlinear dielectric constant depends on the order of the phase transition with a ferroelectric order parameter [1]. In the SmC<sub>A</sub>\* phase, no relaxation is observed in the linear spectrum at the low frequency region, but the third-order nonlinear spectrum shows a Debye-type single relaxation at a few kHz corresponding to the antiferroelectric Goldstone mode. In the SmC\* phase, we have obtained the third-order nonlinear spectrum of a higher-order Debye type with a negative increment, which corresponds to the ferroelectric Goldstone mode [2]. It is also found that all these spectra are explainable by a simple phenomenological model and we can obtain more detailed information on the dynamics of antiferroelectric liquid crystals by the comparison between theoretical and experimental results. This shows the usefulness of the nonlinear dielectric relaxation spectroscopy for studying antiferroelectric liquid crystals.

[1] Y. Kimura and R. Hayakawa, Mol. Cryst. Liq. Cryst., 261, 225 (1995). [2] Y. Kimura and R. Hayakawa, Jpn. J. Appl. Phys., 32, 4571 (1993).

C1P.39

RELAXATION PROCESSES IN THE VARIOUS PHASES OF ANTIFERROELECTRIC LIQUID CRYSTALS USING DIELECTRIC SPECTROSCOPY, F. Bibonne, H. Fredon, <u>J. P. Parneix</u>, H. T. Nguyen \*, V. Faye \*, Laboratoire PIOM, CNRS., Avenue Pey Berland, BP 108, 33402 Talence Cedex, FRANCE, (\*) Centre de Recherche Paul Pascal, CNRS, Avenue A. Schweitzer, 33600 Pessac Cedex, FRANCE.

In previous paper [1], dielectric behaviour of a new antiferroelectric liquid crystal have been investigated. Here, we report dielectric properties for the whole series  $C_nH_{2n+1}O$ - $\varphi$ - $CO_2$ - $\varphi$ - $CO_2$ - $\varphi$ - $CO_2$ - $C^*H(CH_3)C_6H_{13}$  with n=8-12, following the transitions K -  $SmC_A^*$  -  $SmC_{FII}^*$  -  $SmC_{FI2}^*$  -  $SmC^*$  -  $SmC_\alpha^*$  - SmA - I, where  $SmC_\alpha^*$  phase disappears in homologs n=11 and 12, as well as for the coumpound  $C_{12}H_{25}CO_2$ - $\varphi$ -C=C- $\varphi$ - $CO_2$ - $\varphi$ - $CO_2$ - $C^*H(C_2H_5)C_6H_{13}$  which undergoes a phase sequence K -  $SmC_A^*$  - SmA - I. Measurements have been carried out in the frequency range between  $10^2$  Hz and  $10^7$  Hz, under bias field strengths up to 35V.

[1] F. Bibonne, J. P. Parneix, N. Isaert, G. Joly, H.T. Nguyen, A. Bouchta, C. Destrade, Mol. Cryst. Liq. Cryst., 263, 27-35, (1995).



POLAR LOW FREQUENCY MODE IN ANTIFERROELECTRIC LIQUID CRYSTALS, B. Žekš and M. Čepič, Institute of Biophysics, Medical Faculty, Lipičeva 2, 1105 Ljubljana Slovenia

After discovery of antiferroelectric liquid crystals [1], different phenomenological models taking into account interactions between layers have been proposed [2,3]. In the case of non-competing interlayer interactions all models are equivalent; structures and properties of the phases are the same as well as the number and properties of the modes.

In this report we analyse the dispersion relations in the antiferroelectric liquid crystal that exhibits only antiferoelectric  $SmC_A^*$  phase and can be described by the discrete phenomenological model with noncompeting interactions [3]. In these systems two phase modes - antiferroelectric and ferroelectric - and two amplitude modes - also antiferroelectric and ferroelectric - exist. The low frequency antiferroelectric phase mode has very low polarization in comparison to the ferroelectric polar phase mode, which appears at higher frequencies. Both modes are detectable by dielectric means and the main distinction between them is, that in spite of very low frequency of the antiferroelectric phase mode, its susceptibility is lower than the susceptibility of higher frequency ferroelectric phase mode.

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# C1P.41

GENERALIZED DYNAMIC SHAPE ANALYSIS OF POLARIZATION DOMAINS IN FERRO-ELECTRIC LIQUID CRYSTALS, Qi Jiang, Joseph E. Maclennan, Fabien Durringer, and Noel A. Clark, Department of Physics, University of Colorado, Boulder, CO 80309, USA

The electro-optic response of chevron surface-stabilized ferroelectric liquid crystal (SSFLC) cells is principally determined by polarization switching at the chevron interface. We have developed an analytical algorithm analogous to the Wulff construction for calculating the evolution of a class of 2D domains growing from arbitrary starting shapes. The algorithm enables us to derive the full 2D shapes of SSFLC polarization domains with curved walls from the directional variation of the velocity of planar walls as measured by computer simulations. This model predicts that the aspect ratio of the domains is determined mainly by the Frank elastic anisotropy and provides a mathematical criterion for the occurrence of cusps. We have also developed a self-consistent formalism relating the domain shape to the velocity profile of "speedboat" domains in chevron SSFLC cells which we have applied to the analysis of dynamic polarization reversal data obtained as a function of voltage for several FLC materials using video microscopy.

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## C1P.42

A PROBE INTO THE DC BIAS FIELD DEPENDENCE OF THE β-RELAXATION IN VARIOUS ANTIFERROELECTRIC SUBPHASES; H. Xu and F. Kremer, Falculty of Physics, Leipzig University, 04103 Leipzig, Germany, D. Moro and G. Heppke, Technical University of Berlin, I.-N.-Stranski-Institute, D-10623 Berlin, Germany.

The  $\beta$ -relaxation is assigned to the hindered librational motion of the mesogene around its long molecular axis[1]. Because the angular distribution of the lateral dipole moment in ferroelectric, ferrielectric and various antiferroelectric subphases is anisotropic, by superimposing a dc bias field, the aspect angle of the dipole moment interacting with the outer electric field can be varied. As a result, a pronounced dc-bias field dependence of the dielectric strength is observed, which reflects the molecular packing of liquid crystals in the different antiferroelectric subphases, such as  $S_m C^*_{\alpha}$ ,  $S_m C^*_{\gamma}$ ,  $S_m C_A$ , FI and AF phases. This enables to estimate the correlation length of the librational fluctuations of the mesogenes in the different subphases. Our results are discussed with respect to recent electro-optical measurements[2].

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CHOLESTERIC LIQUID CRYSTAL BASED MULTI-LAYER OPTICAL STORAGE TECHNOLOGY, Wolfgang Schlichting, Sadeg Faris, Le Li, Bunsen Fan and John Kralik, John Haag, Zhijian Lu, Reveo, Inc. 8 Skyline Drive Hawthorne, NY 10532, USA

A novel approach to optical storage based on layering of cholesteric liquid crystal (CLC) media has been proposed by Reveo, Inc. CLC media have been chosen due to their unique property of selective reflection, wherein a CLC film reflects light of its characteristic wavelength and polarization handedness at near-zero loss while transmitting all other light. High contrast data patterns are created by selectively crosslinking 1 µm size "1" and "0" data marks in the planar and the isotropic states, respectively. Recording "1" marks is accomplished by scanning a modulated UV laser beam over the CLC disk which is heated to 90 °C. The "0" marks are then crosslinked by heating the disk above the isotropic transition temperature and flooding it with UV light. Individual layers are addressed by tuning the read-out laser to the reflection wavelength and polarization. Up to 400 CLC layers can potentially be stacked on a single disk, which leads ultimately to a single disk capacity of one terabyte. Thus, the capacity is enhanced by a factor of 400 with respect to single layer optical disks, such as CDs. The novel concept has been demonstrated in a 6-layer experiment. This, along with computer simulation indicate that the technology is viable and can go to market earlier than other storage technologies.

C1P.44

LIQUID CRYSTAL DISPLAYS FROM CONDUCTING POLYMER SUBSTRATES, R. Shashidhar, Ling Huang, Liz O'Ferrall, J. Calvert, W. Fritz and J.W. Doane, Code 6900, Naval Research Laboratory, Washington DC 20375 and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242.

Liquid crystal displays (LCDs) are typically fabricated using glass substrates with a coating of indium tin oxide (ITO) which allows for the application of an electric field to the liquid crystal. For many areas of applications there is a need for a LCD with a plastic substrate. We have developed conducting polymer films, which when deposited on different types of polymer substrates, exhibit electrical conductivity and optical properties that are suitable for LCD application. Preliminary results on a cholesteric reflective display are presented and its electro-optic performance is compared to that of ITO-glass based LCDs.

C1P.45

OPTICAL PROPERTIES OF SINGLE LAYER NON-ABSORPTIVE SUPER BROADBAND CLC POLARIZERS, Z. -J. Lu, L. Li and S. M. Faris, Reveo, Inc., 8 Skyline Drive, Hawthorne, NY 10532

Single layer broadband polarizers are of great importance for various optical devices and flat panel displays. Broad band polarizers based on cholesteric liquid crystals (CLC) have been reported by both Reveo and Philips research groups[1,2]. In this paper, we report the results of theoretical study on the optical properties of thus made broadband polarizers. Berreman's 4x4 matrix is used in the simulation of the reflection spectra. Both nonlinear and linear pitch distributions across the cell thickness are used in the simulation and their effect on the bandwidth and reflectivity is assessed. The effect of incident angle on the extinction ratio is systematically evaluated. The film thickness is optimized for the best performance of the broadband polarizers with regard to extinction ratio, reflectivity, and bandwidth. The theoretical results have been compared with the experimental results of Reveo's super broadband polarizers ( $\Delta\lambda \ge 600nm$ ) and shows very good agreement. The theoretical work provides beneficial guidance for the manufacturing of high quality single layer broadband polarizers.

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- 2. D. J. Broer, J. Lub, European Patent #94200026.6, 1994



A Nd<sup>3+</sup>-DOPED SILICA FIBER-LASER USING A CHOLESTERIC LIQUID CRYSTAL MIRROR, C. Li, P. Carette, and M. Warenghem, Faculté des Sciences J. Perrin, Université d'Artois, Lens,62307, France.

A Nd<sup>3+</sup> doped silca fiber is known to lase using only its cleaved input and output ends as cavity mirrors, although with a low lasing efficiency. In this paper we report such a fiber laser with a cholestreric liquid crystal (CLC) mirror butting the input end of the fiber. Besides an obvious enhancement of the lasing action, it is possible to tune the laser wavelength by changing the CLC mirror parameters: temperature, thickness, pitch and the pump wavelength as well. The slope efficiency of the laser is reported in both cases, with and without CLC mirror. The output spectrum of the laser with CLC mirror is studied: the appearance of three different lines is reported depending on both the pump wavelength and the CLC mirror characteristics. Finally the polarization of the output beam is investigated.

## C1P.47

SWITCHING PHENOMENA IN LIQUID CRYSTAL DEVICES FOR INFRARED APPLICATIONS Ian Mason and Guy Bryan-Brown, Liquid Crystal research division, Defence Research Agency, St Andrews Road, Gt Malvern, Worcestershire, UK.

Liquid crystal devices have been proposed for use at infrared wavelengths. These proposals have included several forms of liquid crystal based device<sup>1</sup>. Liquid crystal devices designed for this region need to be considerably thicker than those for use at visible wavelengths<sup>2</sup>.

It has been reported that even in thin LC devices there is evidence of interelectrode switching reducing device performance<sup>3</sup>. This is considered to be due to fringing fields between electrodes. Infrared LC devices being thicker will suffer these effects to a greater degree. In our work we have designed and fabricated liquid crystal devices that operate in the infrared. We report here on our work studying the electro-optical response of the liquid crystal within these devices with special reference to fringing electrical fields.

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#### C1P.48

BRIGHTNESS ENHANCEMENT OF PROJECTION AND DIRECT VIEW DISPLAYS USING CHOLESTERIC LIQUID CRYSTAL FILMS, <u>J.C. Kralik</u>, B. Fan, L. Li and S.M. Faris, Reveo, Inc., 8 Skyline Dr., Hawthorne, NY 10532

Many projection and direct view displays utilize polarized light for operation of their light valve components. These displays utilize dichroic or prism polarizers; however, each of these suffers from inherent deficiencies. Dichroic polarizers have low transmittance, absorbing >50% of incident light; while prism polarizers increase the numerical aperture (N.A.) of an optical system. Planar texture cholesteric liquid crystal (CLC) films are unique in that, in certain configurations, they can polarize a light beam without absorption and without increasing the N.A. of an optical system. We present experimental results and analyses for representative direct view and projection displays which incorporate CLC films for brightness enhancement. We demonstrate a 40-70% brightness enhancement across the face of a conventional LCD backlight that incorporates a polarizer comprised of red-, green- and blue-reflecting CLC films. We also examine the merits of several different types of CLC materials and discuss how they affect display performance and cost. In particular, we discuss the application of a novel, low cost broadband CLC material to LCD backlights.

POLYIMIDE THICKNESS INDUCED ALIGNMENT TRANSITION IN CHOLESTERIC DISPLAYS, J. Ruth, P. Bos, D. Davis, B. Taheri, A. Ali, A. Kahn, X.-Y. Huang, M. Stefanov; Liquid Crystal Institute, Kent State University, Kent OH 44242, USA, Kent Display Systems, Inc., 343 Portage Blvd. Kent OH 44240, USA.

We have investigated the effect of different polyimide alignment layers on the optical and switching properties of reflective bistable cholesteric LCDs. Certain polyimides are found to undergo an alignment transition, from homogeneous to homeotropic, with increasing layer thickness. The optical properties of the LCDs are correlated with this transition. The anchoring of one such polyimide is compared with another polyimide which does not undergo an alignment transition.

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C1P.50

A NEW MODIFICATION OF LC GOGGLES WITH LOCAL SPATIAL MODULATION OF BLINDING OBJECTS, M.G.Tomilin, A.P.Onokhov, N.T.Firsov. S.I.Vavilov State Optical Institute, 199034, St.Petersburg, Birzhevaya Line 12, Russia.

The design principle of the binocular goggles with local light modulation is based on the application of two light-addressed spatial-temporal light modulators (SLMs) placed in optical scheme. The modulators are essentially a "sandwich" structure consisting of the ZnSe semiconductor electrode layer adjacent to the LC layer deposited on the glass plane with operating in the transmission mode therefor the photoconductor based on polycrystalline or monocrystalline ZnSe having the maximum transmission in the visible region is used [1]. When SLMs are placed in the intermediate image plane of the optical system the local modulation is carried out automatically wherever the blinding source is located in the field of view. The main disadvantage of goggles are the unindentical parameters of two different SLMs and their high price. We developed a new modification of goggles based on one SLM with improved parameters and reduced price. The main goggles's characteristics and field of application are discussed.

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C1P.51

CLC-BASED NON-ABSORPTIVE SUPER BROADBAND POLARIZER, Le Li, Zhijian Lu, Yingqiu Jiang, and Sadeg M. Faris. Reveo, Inc., 8 Skyline Dr., Hawthorne, NY 10532.

Single layer non-absorptive polarizers are important in many applications. Reveo [1] and Philips [2] independently invented methods for creating non-absorptive polarizers from cholesteric liquid crystals (CLC). Here, systematic experimental researches will be reported based on Reveo's broadband polarizer which is a CLC blend containing at least one polymer and non-crosslinkable liquid crystal compound(s). Effects by different CLC polymers, nematics, chiral additives, photo initiator percentages, processing temperatures, and polymerization rate have been examined. The bandwidth can be controlled from a few hundred nanometer to thousands of nanometer in a 20 µm thick film with a center wavelength arbitrarily tuned from near UV to near infrared. The resulted polarizer can stand high temperature until 170 °C. A model termed as "Polymerization Induced Molecule Re-Distribution (PIMRD)" has been proposed. The molecule diffusion and redistribution has been experimentally monitored with laser probing beams. A non-linear pitch distribution across the thickness has been observed by an atomic force microscope (AFM).

- 1. Le Li, and Sadeg M. Faris, Novel Single Layer Super Broadband Reflective Polarizer, SID'96.
- 2. D. J. Broer, J. Lub, European Patent #94200026.6, 1996.



# THE EFFECT OF POLYMER NETWORKS ON THE ELECTRO-DISTORTIONAL CHARACTERISTICS OF NEMATIC LIQUID CRYSTALS

J. Li, J. Anderson, C.D. Hoke and P.J. Bos, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

Multi-functional monomers have been used to mix with nematic liquid crystals and form polymer networks to improve the display characteristics. 1,2,3,4 In this study, we investigate the interactions between the formed polymer networks and liquid crystal directors. Assuming the networks are distributed uniformly, the contribution from polymer network to the system free energy is added in the form of  $-\frac{1}{2}K_a(\hat{n} \cdot \hat{N})^2$ , where  $K_a$ ,  $\hat{n}$  and  $\hat{N}$  are polymer network coefficient, liquid crystal director and polymer network unit vector, respectively. Ignoring the polymer networks elasticity, the liquid crystal director configuration and elastic energy under the influence of an external electric field are calculated numerically. The obtained electro-distortional characteristics are found to depend on the value of  $K_a$ . The results are compared to the electro-optic threshold and hysteresis behaviors of a set of highly twisted nematic cells with different monomer concentrations.

Research supported by NSF ALCOM Center under the grant # DMR 89-20147

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## C1P.53

DIELECTRIC RELAXATION OF LOW DIELECTRIC CROSS-OVER FREQUENCY NEMATIC MIXTURES AND THEIR APPLICATION, M. Xu and D.-K. Yang\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242, U.S.A.

We constructed nematic liquid crystal mixtures using components with different dielectric cross-over frequencies. The dielectric anisotropy of one of the component changes from positive to negative at a low cross-over frequency (~3 kHz). The dielectric anisotropy of the other component is negative and does not change for frequencies below 1 MHz. The dielectric cross-over frequency  $f_c$  of the mixture was determined using the threshold in Frederick transition and dielectric spectroscopy. Our results show that the cross-over frequency  $f_c$  of the mixture was shifted a higher value due to the decrease of the viscosity. The dielectric anisotropy was measured at various frequencies at both side of the cross-over frequency. The Our results show that the simple additivity law of dielectric constants of the components does not valid at frequency near the cross-over frequency  $f_c$ . Using the nematic mixture and chiral dopants, we made dual frequency addressed switchable cholesteric polarizers.

# \*Soppurted by Meadowlark Optics

# C1P.54

CURRENT-VOLTAGE CHARACTERISTICS OF MIM ELEMENT AND ITS NEW FORMULA, Hongwu Liu, Jianxing Guo, Zhengjun Ma, Kai Ma, Ximin Huang ,Changchun Institute of Physics , Chinese Academy of Sciences , Changchung 130021

The current-voltage characteristics of a MIM(Metal-Insulate-Metal) switching element in the TFD-LCD could not be described accurately by the conventional Poole-Frankel equation. And it is difficult to estimate and optimize various parameters by the conventional equation, so the optimization of the parameters has been required many experiments with much effort. We give a new formula from the band theory and some experimental formulas to fit the experimental current-voltage characteristics[1] [1] T.Hirai,etal.,ASIA DISPLAY'95 453 (19)

PHOTO-ASYMMETRIC SYNTHESIS OF HELICENES IN LIQUID CRYSTALS, Yuhui Lin and L.-C. Chien,\* Liquid Crystal Institute, chemical Physics and NSF ALCOM Center, Kent State University, Kent, OH 44242

Photo-asymmetric synthesis of pentahelicenes have been carried out in liquid crystals. The objective of this investigation is to study the feasibility of using polyhelicenes as tunable chiral materials in the color pixelization of reflective cholesteric displays (RCDs). Since the pitch of cholesteric liquid crystal phases can be changed by the addition of a small amount of chiral compound, *in-situ* photo-asymmetric synthesis in display cells provides a valuable method in the modification of liquid crystal properties. We describe herein attempts to use photoirradiation to modify the pitch and hence, the color of a RCD. The synthesis of helicene precursors 1, 2-di-(2-naphthyl)ethylene and 1-(6-methoxy-2-naphthyl)-2-(2-naphthyl)ethylene will be presented. The asymmetric photo-reaction of these compounds in cholesteric red mixture with unpolarized, linearly polarized, and circular polarized light will be demonstrated.

This research was supported in part by the APPA Low power Displays Contract # N61331-94-K-0042.

C1P.56

ANGULAR DEPENDENCES OF PRISM LIQUID CRYSTAL POLARIZER. A.A.Karetnikov<sup>†</sup>, A.P.Kovahik, Y.I.Rjumtsev, <sup>†</sup>S.I.Vavilov State Optical Institute, Birzhevaya Line 12, St.Petersburg, 199034, Russia; Institute of Physics of St.Petersburg University, Ulianovskaya 1, Petrodvorets, St.Petersburg, 198904, Russia.

The field-of-view dependences of linear polarizers [1] are important for different applications that involve noncollimated or off-axis collimated beams. We present here the results of investigations on angular dependence of polarization plane orientation in exit beam and angular dependence of extinction ratio of prism liquid crystal polarizer [2]. The measurements are performed with single-mode He-Ne laser as a source of 632.8 nm wavelength radiation. The homeotropic and planar configurations of NLC layer director are used. The relation between the type of configuration and angular dependances is analysed. The optical properties of NLC layer which appear to be responsible for restriction of extinction ratio, are discussed. The comparision with multilayer polarizing beam-splitter cubes is given.

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C1P.57

CHOLESTERIC LIQUID CRYSTAL BASED BEAM STEERING DEVICE Sanjay Tripathi, Hemasiri Vithana, and S. M. Faris, Reveo, Inc. 8 Skyline Drive, Hawthorne NY 10532

High speed scanning/deflection of monochromatic laser beams is essential to advanced optical systems and require random and or sequential scanning of laser spot over an image plane. We have developed a beam steering device (BSD) based on a micro-miniature polarization BSD element which either transmits or reflects a beam of light based on its polarization.

This invention exploits unique optical properties of cross linkable cholesteric liquid crystal (CLC) silicones. These CLC's are polarization sensitive, they reflect right circularly polarized light and transmits left circularly polarized light or *vice versa*. The CLC, with a phase shifter ( $\pi$ -cell), can be used to make a basic building block of a scanner/electro-optical crossbar switch. This solid state device is compact, operates in microsecond second range at ~30 Volts (possibly less). The operating principle and possibly a prototype will be presented.



FLUCTUATION IN ANTIFERROELECTRIC SMECTIC PHASES AS OBSERVED BY ELECTROOPTIC METHODS, <u>Kazuyuki Hiraoka</u> and Yoshiko Uematsu, Tokyo Institute of Polytechnics, 1583 Iiyama, Atsugi-shi, Kanagawa 243-02, Japan

In order to investigate the molecular fluctuation behavior of the chiral smectic phases possessing antiferroelectric ordering, we have carried out electrooptic measurements in 4-(1-methylheptyloxy-carbonyl)phenyl-4'-octyloxybiphenyl- 4-carboxylate which has two antiferroelectric smectic phases, namely  $SmC\alpha^*$  and  $SmC_A^*$ . We confirmed the relaxation corresponding to the ferroelectric phase mode in the  $SmC\alpha^*$  phase by measuring the linear and second harmonic responses of electro-optical signal under a sinusoidal electric wave. Though the relaxation of the helical fluctuation due to the antiferroelectric phase mode, which is corresponding with the symmetry-recovering Goldstone mode, was clearly observed in  $SmC_A^*[1]$ , no evidence about helical fluctuation was confirmed in the  $SmC\alpha^*$  phase. In addition, the molecular interactions between two adjacent layers in the  $SmC_A^*$  and  $SmC\alpha^*$  phases are discussed. [1] K. HIRAOKA *et al.*, Ferroelectrics, 147 (1993) 13.

# C1P.59

POLARIZATION PROPERTIES OF A LIQUID CRYSTAL PHASE GRATING, Zhan He, Toshiaki Nose, and Susumu Sato, Department of Electrical & Electronic Engineering., Akita University, 1-1 Tegatagakuen-cho, Akita 010, Japan.

By measuring Stokes' parameters of diffraction light versus the applied voltage, polarization and diffraction properties of a liquid crystal (LC) phase grating are investigated, where LC molecules are treated to have a homogeneous alignment parallel to grating electrode direction. A transparent ITO grating electrode structure is used to yield a periodic electric field. When a voltage above the threshold is applied, polarization states of diffraction light can be varied, as well as diffraction light intensities. If a linearly polarized light whose polarization direction is parallel or perpendicular to the grating direction is incident onto the LC grating, we have, at first time, demonstrated experimentally symmetric diffraction light intensities and antisymmetric polarization properties in corresponding negative and positive orders, e.g. the major axes and rotation directions of diffraction light ellipse are antisymmetric. The reason of the unique polarization property is considered to be at least related to the inverse twisted domains induced by the inhomogeneous electric field. Moreover, due to the phase grating structure, diffraction efficiencies and contrast ratios of diffraction light are much higher. Such the LC grating is expected to have potential applications in optical computing, interconnect and switching.

#### C1P.60

OPTICALLY ADDRESSED SPATIAL LIGHT MODULATORS USING DEFORMED HELIX FERROELECTRIC LIQUID CRYSTALS (DHF LC OASLM), A.P.Onokhov, <u>L.A.Beresnev</u>\*, W.Dultz#, N.I.Ivanova, A.N.Chaika, A.L.Gromadin§, and W.Haase\*, S.I.Vavilov Center "GOI", Birgevaya Liniya, 12, St.Petersburg, Russia, \*Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, 64287 Darmstadt, Germany, #Deutsche Telekom AG, Am Kavalleriesand 3, 64276 Darmstadt, Germany, Institute of Rear Metalls "GIREDMET", Moscow Russia.

We have developed the DHF LC OASLM's based on photoconductive  $\alpha$ -Si:H film in photodiode p-i-n configuration [1]. The performances of the developed devices are presented. Parameters of the developed DHF FLC material: pitch of helix  $p_0 < 0.3 \mu m$ , spontaneous polarization  $P_s = 200 n C cm^{-2}$ , tilt angle  $\Theta_0 = 31^{\circ}$ , response time less 200  $\mu s$ , thickness of FLC layer  $6 \mu m$ . The holographic technique was used for measuring the diffraction efficiency and spatial resolution. The maximum efficiency was obtained for white light with intensity as low as  $8.10^{-6} \ W cm^2$ . The frequency range of operation was found 1Hz - 5kHz for spatial resolution 45 mm<sup>-1</sup>. The dependences of the diffraction efficiency on the write beam intensity, on the driving voltage frequency and on the spatial frequency of the holographic grating are presented.

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OPTICAL LIMITING DEVICES BASED ON PHOTOADDRESSED SPATIAL LIGHT MODULATORS, USING FERROELECTRIC LIQUID CRYSTALS, <u>L.A.Beresnev</u>, W.Dultz#, A.P.Onokhov, and W.Haase, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, 64287 Darmstadt, Germany, #Deutsche Telekom AG, Am Kavalleriesand 3, 64276 Darmstadt Germany, \*Optical Research & Development Company "PeterLab, Ltd.", Lomonosova str.,5, 194011 St.Petersburg, Russia

The problem of protection of eyes or video camera (optical limiting) takes place at gas cutting, welding, observation of images at very strong spurious light. The local discrimination of light intensity of strongly illuminated images in the field of view without suppression of brightness of images with weak illumination is among the best solution of this goal. We present the modell sample of optical limiting device, based on optically addressed spatial light modulator (OASLM), using ferroelectric liquid crystal. In this device the semi-transparent ZnSe film with thickness  $1\mu m$  is used as a photoconductive layer. The deformed helical ferroelectric liquid crystal is used as a light modulating layer. The sensitivity of developed OASLM is of order  $1-10\mu Wcm^{-2}$ , spatial resolution: of order 100 lp/mm, operation frequency: in the range of hundreds Herz. The operation of device is demonstrated for protection of eye or video camera by means of local suppression of light intensity of lamp or sun image (spurious background) without strong suppression of the weakly illuminated image.

Support from Volkswagen-Stiftung, Project I/70668, and Deutsche Telekom AG is gratefully acknowledged.

C1P.62

DEVELOPMENT OF NON-BIREFRINGENT OPTICAL ADHESIVES,\* <u>D. Nwabunma</u> and T. Kyu, Department of Polymer Engineering, The University of Akron, Akron, Ohio 44325, USA.

The birefringence compensation technique has been employed through polymer blending for the development of non-birefringent optical adhesives. It was found that trimellitic anhydride (TMA) cured polymethyl methacrylate (PMMA)/Epoxy (EPON-828) system resulted in phase separation during polymerization. To circumvent the problem of polymerization induced phase separation, a copolymer system comprised of methyl methacrylate and gylcidyl methacrylate (MMA-co-GMA) was synthesized and blended with EPON-828 then cured thermally with TMA. The cured blend films showed a single glass transition at all compositions and optical transparency, suggestive of miscible character. These optical adhesive blends showed zero birefringence at compositions between 60-70 wt% copolymers. The zero birefringence afforded by the compensation of the opposite intrinsic birefringence of the constituent polymer chains may be attributed to the complete miscibility of the blends in the cured state.

\* Supported by Ohio Board of Regents and NSF-ALCOM Grant No. DMR 89-20147.

C1P.66

NUMERICAL CALCULATIONS ON A DISCRETE MODEL EXHIBITING FERRO-,FER RI-AND ANTIFERRO-PHASES, Arun Roy and N.V.Madhusudana, Raman Research Institute, Bangalore 560 080, INDIA.

Numerical calculations on a modified version of the Orihara-Ishibashi[1,2] model of antiferroelectric liquid crystals are presented. In our discrete model the nearest neighbour interaction changes sign as the temperature is lowered, while the second neighbour interaction remains antiferroelectric. The free energy of the N layer system (N  $\sim$  100 to 300) is minimised by using an appropriate relaxation technique. Introducing suitable chiral interactions, we can get first order SmC\* - FI<sub>H</sub> - 4 layer Antiferroelectric- FI<sub>L</sub> - SmC<sub>A</sub> phase transitions. |  $\Delta \phi$  | the difference in the azimuthal angle between successive layers, is between 0 and  $\pi/2$  in FI<sub>H</sub> and  $\pi/2$  and  $\pi$  in FI<sub>L</sub> phases. Unlike in the earlier models [1,2], we do not require unit cells made of 2 layers to describe FI phases.

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ELECTRO-OPTICAL AND DIELECTRIC BEHAVIOUR OF THE HOMOLOGOUS SERIES MHPnCBC, G. Heppke, D. Lötzsch, J. Nolte-Bömelburg and S. Rauch, Iwan N. Stranski Institute, Technische Universität Berlin, Sekr. ER 11, Straße des 17. Juni 135, D-10623 Berlin

The homologous series MHPnCBC has been synthesized ( $n=7\dots18$ ; compound n=8 has been described earlier [1]). Polymorphy and phase transition temperatures will be presented. Besides  $\mathrm{SmC}_{\gamma}$  and  $\mathrm{SmC}_{\alpha}$  the occurence of a third chiral induced phase ( $\mathrm{SmC}_{x}$ ) which shows a texture similar to the  $\mathrm{SmC}_{\gamma}$  phase is established. Electro-optical and dielectric investigations have been performed

(I) to study the influence of the length of the achiral side chain on the ferri- and antiferroelectric properties (II) to characterize the nature of the third chiral induced phase  $(SmC_x)$ .

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## C1P.68

POLARIZATION CROSSTALK FOR CHOLESTERIC LIQUID CRYSTAL FILMS AT OBLIQUE ANGLES OF INCIDENCE, <u>John.C. Kralik</u>, Hemasiri. Vithana, Sanjay. Tripathi and Sadeg.M. Faris, Reveo, Inc., 8 Skyline Dr., Hawthorne, NY 10532

We investigate crosstalk in reflection from and transmission through cholesteric liquid crystal (CLC) films for polarized light at oblique angles of incidence. We show both experimentally and numerically that the degree of crosstalk is a function of normalized CLC birefringence,  $\Delta n/n$ , and on CLC film thickness, L/p. Here,  $\Delta n/n$  is the ratio of birefringence to average index and L/p is the ratio of film thickness to CLC pitch. For CLC polymers with  $\Delta n/n=0.10$ , and  $L\sim10p$ , there is little crosstalk at a 45° angle of incidence; however, for a low molecular weight CLC with  $\Delta n/n=0.144$  and the same thickness, there is significant crosstalk between the two circular polarization states. The experimental results are compared with numerical results generated by a Berreman's code and found to give good agreement. We present these results and discuss their implications for applications of CLC films as dichroic polarizers, in displays and in related optical technologies.

## C1P.69

ANTIFERROELECTRIC AND FERROELECTRIC LOW MOLAR MASS LIQUID CRYSTALS, W. K. Robinson, R. J. Campin, P. Kloess, H. J. Coles, Liquid Crystal Group, Physics Department, Southampton University, Southampton, SO17 1BJ, UK.

It is well known that both the mesomorphic behaviour and the physical properties of liquid crystalline organosiloxanes can be tuned by modifying the shape of the siloxane group. These smaller oligomeric siloxane units exhibit properties typical of polymers, such as low glass transition temperatures, because they are able to build a 'virtual' siloxane backbone like that seen in a polysiloxane polymer. The advantage of these materials is that it is possible to optimise the backbone properties to give mechanical stability whilst at the same time retaining the electro-optic properties of LMM materials. We monitored the influence of increasing siloxane length on the electro-optic properties of a series of mono- and bi-mesogenic compounds. All compounds exhibited either broad ferroelectric or antiferroelectric phases with high tilt angles (~45°) and Ps (~100nC/cm²). The siloxane does not appear to alter the phase range or the transition temperatures.

NEMATIC BEND-SPLAY ELASTICITY OF CYANOPHENYL COMPOUNDS WITH DIFFERENT TERMINAL GROUPS, I.P.Kolomiets\*, S.K.Filippov, A.M.Ovsipyan, Department of Physics, St. Petersburg State University, St. Petersburg, 198904 RUSSIA.

The bend and splay elastic constants determined by the Freedericksz method in the nematic phase of six homologues of p-n-alkoxy-cyanophenyl bensoates (CPB<sub>n</sub>) with number of CH<sub>2</sub> groups n (n=5 - 10) and three cyanobiphenyl esters with following terminal groups: C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>10</sub>-(CH<sub>2</sub>)<sub>n</sub>-COO- (CBH<sub>n</sub>, n=0, 2) and C<sub>7</sub>H<sub>15</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>3</sub>-COO- (CBP) are reported. The nematic elasticity of the investigated compounds exhibits following features: splay constant of odd homologues CPB<sub>n</sub> is larger in comparison with even those; the temperature dependence of the splay constant of CBH<sub>0</sub> has nonmonotonic character. CBH<sub>2</sub>, CBP<sub>9</sub> and CBP<sub>10</sub> exhibit smectic phases and pretransitional increasing of bend constant near nematic-smectic transition point. In vicinity of transition the appearance of periodical deformation in magnetic field was found. This deformation can be frozen in smectic phase. The critical behaviour of the bend constant is discussed.

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C2P.04

STEP-BY-STEP THINNING OF FREE-STANDING FILMS ABOVE SmA-N and SmA-iso TRANSITIONS, E.I. DEMIKHOV \*\* and V.K. DOLGANOV \*, \* Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia; \* Institute of Physical Chemistry, University of Paderborn, 33095 Paderborn, Germany

Regular decrease of the free-standing film thickness on heating above the transition temperatures SmA - N, SmA - isotropic is observed. The film thickness can be described in studied substances by a power law function of temperature:  $d \propto ((T-T_c)/T_c)^{-\nu}$ , where  $T_c$  is A-N or A-iso transition temperature and  $\nu$ =0.8±0.1. These results can be explained by the phenomena of surface ordering. Usually the boundary layers are more ordered with respect to the films interior. Free-standing films are stable in the nematic or isotropic temperature intervals, if the film thickness equals to double penetration length of smectic A-like surface order. The step-by-step thinning is an untrivial melting process of the surface ordered regions taking place in the films interior. The nematic phase is formed inside the films and removed to the meniscus to eliminate the additional contribution to the free energy on the boundary SmA - Nem. The value of  $\nu$  correlates with the exponent describing the power law temperature dependence of the smectic correlation length in the nematic phase  $\nu$ ||.

[1]. E.I. Demikhov, V.K. Dolganov and K.P. Meletov, Phys. Rev. E 52, 1285 (1995); E.I. Demikhov and V.K. Dolganov, to be published in the Proc. of the 5th Int. Ferroelectric LC conference, Ferroelectrics (1996).

C2P.05

## TILT INDUCED PHASE TRANSITIONS IN HEXATIC SYSTEMS,

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\* Department of Physics, Warsaw Technical University, Poland

The phase transitions between the orthogonal and tilted hexatic phases has been found to exhibit the mean-field behavior. The β critical exponent for the tilt order parameter close to 0.25 was determined in compounds with the HexB - SmF and reversed SmF - HexB phase sequences. Both the phase transitions between the hexatic phases are accompanied by small c<sub>p</sub> jump (0.1 Jg<sup>-1</sup> K<sup>-1</sup>). Moreover, the tricritical points induced by the crystalline fluctuations from the CryB and CryG phases have been shown to exist on the HexB - SmF phase transition line for the systems with the CryB - HexB - SmF and CryG - SmF - HexB phase sequences, respectively.



PHOTO-STIMULATED PHASE TRANSITION IN A MIXTURE OF A NEMATIC LIQUID CRYSTAL AND BACTERIORHODOPSIN, Akihiko Sugimura, Michiyoshi Kuze, \*Ou-Yang Zhong-can, and Tôru Yoshizawa, Dept. of Information Systems Engineering, Osaka Sangyo University, Daito-shi, Osaka 574, Japan, \*Institute of Theoretical Physics, Academia Sinica, P.O.Box 2735, Beijing 100080, China

We have investigated the photo-stimulated phase transition in an emulsion containing a bio-macromolecular purple membrane (PM) in a solution of a low molecular 4-cyano-4'-5-alkyl-biphenyl (5CB). The PM of Halobacterium used in our experiments is composed of bacteriorhodopsin (bR) and lipid. The phase transition temperature (Tc) from a nematic to an isotropic phase decreased with increasing the concentration of PM (0.05, 0.1, 0.5, and 1.0 weight %) under dark conditions. On a light illumination to the mixture for several seconds, Tc decreased with increasing the light intensity. This remarkable photo-stimulated effect is based on the photo- isomerization from all-trans to 11-cis of the retinal chromophore of bR due to a photon absorption of bR, which reverts to the original state within several milliseconds. Thus, the molecular size of bR in all-trans would be smaller than that in 11-cis state. On the other hand, the increase of the illumination time made Tc increase. It is now open question what kinds of molecular interactions and/or photo-reactions in a mixture contribute to the changes of Tc. Another noticed result is that the mixture displayed the patterns like a four-teeth circular saw at a temperature just below Tc under the orthoscopic observation with a microscope. This may be based on an optical activity of the mixture.

#### C2P.07

EXPERIMENTAL PROBES OF THE STRUCTURE OF BLUE PHASE III, V.K. Dolganov\*, Institute of Solid State Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow distr., Russia.

Possible structure of the Blue Phase III are analyzed using spectral and optical measurements, both in bulk samples and in a liquid crystal film. The transmission spectra [1], optical diffraction for various orientations of the scattered wave vector with respect to the direction of the electric field were measured along with the change in the index of refraction. The experimental data were used to determine the magnitude of the duplication index N (i.e., the number of reciprocal-lattice vector  $\tau$  with a given  $|\tau|$ ). The orientational distribution functions of the wave vector connected with diffraction were reconstructed for the Blue Phase III. These data are compared with existing theoretical models of local order in Blue Phase III. The results obtained agree with simple cubic structure proposed by Collings.

[1] V.K.Dolganov, JETP 81, 320 (1995). \*Support by RFFR Grant 95-02-05343.

#### C2P.08

HEAT TRANSPORT ANISOTROPIES IN ALIGNED OCTYLCYANOBIPHENYL (8CB) LIQUID CRYSTAL, M. Marinelli, F. Mercuri, S. Foglietta, U. Zammit and F. Scudieri, Dipartimento di Ingegneria Meccanica, II Università di Roma "Tor Vergata", Via della Ricerca Scientifica 00133, Roma, Italia

The behavior of the specific heat (c), thermal conductivity (k) and thermal diffusivity (D) in the Smectic-A, Nematic and Isotropic phases of aligned 8CB has been studied with the photopyroelectric technique (PPE). The critical behavior of c, k and D has been also determined for different alignments. As expected the specific heat does not depend on the molecular orientation while the thermal transport parameters behavior is substantially different for omeotropic and planar alignment. It has been shown however that the thermal diffusivity critical behaviour is characterized by the same critical exponent in the two cases so that it do not seem to be connected to the absolute values of D. The thermal conductivity remains substantially flat with only a minor increase close to the transition temperature.

CHARACTERISING THE NATURE OF THE SmA-SmC AND SmA-SmC\* TRANSITIONS, L.G. Benguigui and P. Martinoty<sup>†</sup>, Solid State Institute, Technion - Israël Institute of Technology, 32000 Haifa, Israël.

We provide a theoretical explanation of the critical (i.e. non mean-field) behavior of specific heat, as it has recently been observed on certain compounds [1,2]. This explanation rests on the Andereck and Swift free energy [3] introducing terms which couple the order-parameter with both layer-compression and density. We show that the behavior of specific-heat depends on the intensity of these couplings, and that the behaviors which can be observed are therefore of the mean-field, gaussian (ref. 1) or 3DXY (ref. 2)-type.

- [1] L. Reed, T. Stoebe and C.C. Huang, Phys. Rev. E52, 2157 (1995).
- [2] K. Ema, J. Watanabe, A. Takagi and H. Hao, Phys. Rev. E52, 1216 (1995).
- [3] B.S. Andereck and J. Swift, Phys. Rev. A25, 1084 (1982).
- <sup>†</sup> Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, U.R.A. au C.N.R.S. n°851, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France.

C2P.10

ELECTRIC FIELD EFFECT ON THE NEMATIC-ISOTROPIC PHASE TRANSITION FOR SIDE CHAIN LC POLYMER, T.A. Rotinyan, S.G.Kostromin, V.P. Shibaev, Depatment of Physics, St. Petersburg State University, St. Petersburg 198904, Chemistry Department, Moscow State University, Moscow, 119899, Russia.

Pulsed electric fields are used to study the influence of a srtong field up to  $10^7 V/m$  on the nematic-isotropic phase transition for termotropic LC comb-like polyacrylic polymer having cyanobyphenyl groups in side chains. The electric field-induced optical anisotropy is observed and it is shown that such electric fields can shift the transition temperature substantially. The induced birefringence in the isotropic phase and the shift of the transition temperature are measured as a function of the electric field strength. The results are compared with the results for its low-molecular analogs [1].

[1] Rotinyan T.A., Rjumtsev E.I., and al., 1987, Soviet Phys. JETP Lett., 46,331.

C2P.11

CALORIMETRIC AND DILATOMETRIC STUDY ON A BINARY LIQUID CRYSTAL SYSTEM WITH A NEMATIC - SMECTIC A - SMECTIC C POINT - M. Castro, J. A. Puértolas; Dpto Ciencia y Tecnología de Materiales y Fluidos, Centro Politécnico Superior de Ingenieros, 50015 Zaragoza (Spain); B. Heinrich, D. Guillon; Institut de Physique et de Chimie des Matériaux de Strasbourg, 67037 Strasbourg cedex (France)

Several mixtures of two isomers with the phase sequences N-S<sub>A</sub>-S<sub>C</sub> (4-octyloxyphenyl 4'-decyloxybenzoate) and N-S<sub>C</sub> (4-decyloxyphenyl 4'-octyloxybenzoate) are studied by means of high resolution ac calorimetry and dilatometry. A tricritical point is found on the N-S<sub>A</sub> transition line. The S<sub>A</sub>-S<sub>C</sub> transition line, analysed by the extended Landau model, shows a tricritical behaviour tendency close to the N-S<sub>A</sub>-S<sub>C</sub> point; this is consistent with previous results [1,2] and is discussed in the frame of the controversy upon the occurrence of a tricritical point on the S<sub>A</sub>-S<sub>C</sub> transition line [3-5]. The variation of the specific heat with temperature in the nematic phase shows a rounded anomaly for dilutions close to the N-S<sub>A</sub>-S<sub>C</sub> point. The occurrence of this anomaly as well as the influence of the width of the nematic domain [1] are discussed.

[1] J. Zubía and co., Phys Rev. E, 48 (1993) 1970; [2] X. Wen and co., Phys Rev. A, 42 (1990) 6087; [3] H. Y. Liu and co., Phys Rev. A, 40 (1989) 6759; [4] G. Heppke and co., Liq. Cryst., 5 (1989) 489; [5] S. K. Prasad and co., Phys Rev. A, 42 (1990) 2479.

THERMOTROPIC LAMELLAR TO COLUMNAR PHASE TRANSITION, <u>D. Guillon</u>, B. Heinrich, C. Cruz, A.C. Ribeiro, H.T. Nguyen, Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 23 rue du Loess, 67037 Strasbourg Cedex, France

In this work, we present a structural study of the smectic C and columnar hexagonal mesophases exhibited by a biforked molecule. This study was performed by means of X-ray diffraction and dilatometry as a function of temperature. In the smectic C phase, the existence of peristaltic undulations of the rigid cores's sublayer is postulated, with a molecular packing where the rigid parts of the molecules are much more tilted than the terminal aliphatic chains. In the columnar mesophase, the columns are formed by the piling of clusters containing, in average, 4.5 molecules arranged side by side, resulting in a columnar core consistent with the symmetry of the packing. As for the transition between these two mesophases, it is shown that, with increasing temperature, the undulations of the smectic C lamellae are the precursors of the columns, the breaking of the smectic layers occuring when the amplitude of the undulations reaches the whole aromatic sublayer thickness.

## C2P.13

PHASE BEHAVIOUR AND BIREFRINGENCE STUDIES OF A LIQUID CRYSTAL BINARY MIXTURE, M.Mitra\*, S.Sinha Roy, T. Pal Majumder and S.K.Roy, Dept. of Spectroscopy, IACS, Jadavpur, Calcutta-32, India; \*Dept. of Physics, Bangabasi Morning College, 19 Scott Lane, Calcutta-9, India.

The phase behaviour of binary system of 4-n-pentyl 4'-cyanobiphenyl (5CB) and 4-pentyl phenyl trans-4-pentyl cyclohexyl carboxylate has been studied under a polarizing microscope equipped with a Mettler hot stage. The mixtures show the presence of induced smectic A phase (focal conic fan texture). For the second sample we have found that while heating from solid it possesses only nematic phase in the mesophase, but while cooling slowly from isotropic phase it exhibits nematic phase and a higher order smectic phase (Sm G, mosaic texture) before going into the solid state. This higher order smectic phase exists in the binary mixtures of these two samples upto mole fraction of 5CB less than 0.07. Refractive indices and densities for different compositions of this mixture are measured to estimate orientational order parameter. We have used here both Vuks' as well as Neugebauer's model to calculate polarizabilities. Experimental order parameters are compared with McMillan's theory [1] for Sm A phase and Maier-Saupe theory [2] for nematic phase. The changes in different physical parameters with concentrations are discussed.

- [1] W. L. McMillan, Phys. Rev. A4, 1238 (1971); A6, 936 (1972).
- [2] W. Maier and A. Saupe, Z. Naturforsch. 13a, 564 (1958).

# C2P.14

POLYMORPHISM STUDIES OF SOLID ETHOXYBENZYLIDENEPROPYLANILINE, <u>W.Witko</u>\*, A.Bak,# J.Mayer\*, \*-Henryk Niewodniczański Institute of Nuclear Physics, 31-342 Kraków, Poland, #-Chair of Physics, Rzeszów Technical University, 35-959 Rzeszów, Poland.

We have investigated nematogenic 4-ethoxybenzylidene-4'-propylaniline (EBPA) using polarized light optical microscopy and differential scanning calorimetry (DSC) in wide temperature range (180K -380K). Various heating and cooling rates (0.1K/min - 100K/min) were applied to samples with different thermal history.

EBPA is isomeric to widely studied 4-methoxybenzylidene 4'-butylaniline (MBBA) with many solid phases. Slightly modified molecular structure increases melting and clearing temperatures and reduces number of solid modifications. Stable crystal phase melts in 350.0K to nematic phase which can be easily undercooled more than 20 degrees. On cooling of nematic phase metastable solid phase is formed which normally spontaneously transforms into stable one (probably via ferroelastic type phase transition) between 326 and 328K depending upon cooling rate. But the metastable phase can be rapidly cooled to low temperatures and on heating it melts at 345.6K. However on slow heating the formation of stable phase is observed. These studies show the importance of butyl group for MBBA polymorphism.

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OPTICAL STUDY OF THE PHASE TRANSITIONS IN LIQUID CRYSTALS <u>V.Ye. Pogorelov</u>, I.B. Estrela-Llopis, I.P. Pinkevich, V.P. Bukalo, Department of Physics, Kiev T. Shevchenko's University, Kiev, 252127, Ukraine.

The vibrational spectra investigation of mesomorphous materials have been allowed to obtain important information about peculiarities of phase transitions in such objects [1]. The aim of work was to perform the experimental and theoretical analysis of Raman bands forming in various phases. Results of investigation of temperature variations of Raman spectra of preliminary cooled nematic MBBA with different cooling rate (shock, slow and intermediate) are presented in the report. It has been made the analysis of forming mechanisms of Raman bands contours with using of theory of Raman effect in condensed phase. In spite of the difference of heterogeneous broadening nature for nematics and amorphous phases the proximity of Raman bands widths for these phases is stipulated one of parameter of corresponding averaging statistic distributions. Models of structural transformations, possibility of prognostic of structural evolution and identification of phase transitions for wide class of liquid crystals in dependence on their thermal pre-history are discussed in the report.

[1]. V.Ye. Pogorelov, Solid State Physics. 33, 1906 (1991).

C2P.16

HEAT CAPACITY AND OPTICAL REFLECTIVITY STUDIES OF PHASE TRANSITIONS IN 40.8 FREE-STANDING THIN FILMS, A.J. Jin1†, C.C. Huang1\*, C.F. Chou2, C.Y. Chao2, J.T. Ho2\*, S.W. Hui3; 1: Dept. of Physics, University of Minnesota, MPLS, MN 55455; 2: Dept. of Physics, SUNY at Buffalo, Buffalo, NY 14260; 3: Dept. of Biophysics, Roswell Park Cancer Institute, Baffalo, NY 14263; † Current address: Dept. of Physics, CWRU, Cleveland, OH 44106.

By using our high resolution differential ac calorimeter and optical reflectivity setup, free-standing films of the N-(4-n-butyloxybenzylidene)-4-n-octylaniline (4O.8) compound have been carefully studied [1] near its bulk smectic-A - crystal-B transition. Our data reveal an interesting phenomenon. As usual, series of layer-by-layer transitions were observed, but some of heat capacity anomalies display a strong fluctuation contribution. Complementary electron-diffraction studies show that the outermost surface layers, at the least, undergo the liquid-hexatic transition before it establishes the crystalline order. These findings allow us to resolve the discrepancy between our heat capacity results and previous torsional oscillator ones concerning the surface crystalline transition temperature. We have analyzed the heat capacity anomaly associated with the surface transition in detail. Our calorimetry can not resolve any anomaly associated with the hexatic-crystalline transition of the two outermost layers.

[1]: A.J. Jin, T. Stoebe, C.C. Huang; Phys. Rev. E 49, R4791 (1994).

\* Supported by NSF Grant Nos. DMR-93-00781 and 91-03921, respectively.

C2P.17

MONTE-CARLO SIMULATIONS OF HEAT CAPACITY AND HELICITY MODULUS OF A COUPLED XY MODEL IN TWO DIMENSIONS,\* I. M. Jiang, Department of Physics, National Sun Yat-sen University, Kaohsiung, Taiwan, and T. Stoebe, and C. C. Huang, Department of Physics, University of Minnesota, Mpls., MN 55455, USA

In light of recent experimental findings from heat capacity, optical reflectivity and electron-diffraction studies of thin 3(10)OBC liquid-crystal films near the smectic-A-hexatic-B transition, computer simulations have been conducted to obtain a much better understanding of the nature of this intriguing transition. Utilizing Monte-Carlo simulations, we have calculated both the helicity modulus and heat capacity versus temperature of a coupled classical XY model in 2D. Our model system is based on a Hamiltonian first proposed by Bruinsma and Aeppli. The helicity modulus results strengthen our previous report of a new type of phase transition in which two distinct types of order are simultaneously established through a single continuous transition.

[1] I. M. Jiang, T. Stoebe, and C. C. Huang, accepted for publication in Phys., Rev. Lett. \* Supported in part by NSF Grant DMR 93-00781 and National Science Council, Taiwan.



THE TOPOLOGICAL MICROSTRUCTURE OF NEMATIC DEFECTS, <u>P. Bisca-ri</u><sup>(1)</sup>, G. Guidone Peroli<sup>(2)</sup>, and T. J. Sluckin<sup>(3)</sup>. <sup>(1)</sup>Dipartimento di Matematica, Politecnico di Milano, MILANO (Italy); <sup>(2)</sup>Dipartimento di Matematica, PISA (Italy); <sup>(3)</sup>Department of Mathematics, SOUTHAMPTON (England).

We study the core of line and point defects in nematic liquid crystals. The topological theory of defects allows us to prove that a uniaxial nematic has two ways to avoid a topologically stable defect: either it melts, by becoming isotropic on the putative defect, or the following biaxial structure arises. The singular points are substituted by uniaxial points where the sign of the order parameter s gets reversed. These new uniaxial points are surrounded by a biaxial region which encloses a surface where upon one of the eigenvalues of the order parameter tensor **Q** vanishes.

# C2P.19

EFFECTS OF DISPERSED POLYMER NETWORKS ON THE NEMATIC-ISOTROPIC TRANSITION, R.-Q. Ma and D.-K. Yang\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242, U.S.A.

We have constructed a nematic liquid crystal/polymer network system. The polymer network is formed in the nematic phase and is fibril-like. It mimics the order and orientation of the liquid crystal during the polymerization. The polymer network has strong aligning effect on the liquid crystal. We studied the nematic-isotropic phase transition and the polymer network-induced order of the liquid crystal in the isotropic phase. We observed that as the concentration of the polymer network is increased, the discontinuity of the order parameter at the nematic-isotropic transition becomes smaller and eventually disappears. We also observed that the aligning effect of the network depends strongly on the lateral size of the fibrils of the network, which can be controlled by structure of the monomer, the curing temperature and the uv intensity.

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# C2P.20

STRUCTURAL ASPECT OF PHASE TRANSITIONS IN 4 - CYANOPHENYL ETHER - 4'-HEPTYLBENZOIC ACID, <u>S.I.Tatarinov</u>, L.M.Babkov, O.V.Gorshkova, V.I.Berezin, Department of Physics, N.G.Chernishevsky State University, Astrakhanskaya str., 83, Saratov, 410071, Russia

Conformations and their changes in phase transitions C-N-I-solution (S) have been investigated by theoretical and experimental IR spectroscopy methods. IR spectra in the  $400-3200\,cm^{-1}$  region of disordered and oriented layers of the 4 - cyanophenyl ether - 4' - heptylbenzoic acid (CPEHBA, C 46N52 I) were measured as a function of a temperature and unpolar solvent concentrations. The interpretation of spectral changes was obtained by polarization [1] and theoretical analysis on the basis of band assignment in IR spectra of conformations which were calculated by numeric methods. Spectral-structural correlations were found. They were used for the explanation of the structural changes of CPEHBA in C, N, I and S (in  $CCI_4$  to 0.14 wt.p.c.). In all phases the out-of-plan molecular conformations were realised. The rotation anglesof benzoic rings around bonds  $C_w - COO$  and  $C_w - OOC$  were different and decresed for C. In contrast to N, I, S not all-trans but broken forms of alkyl chain exist in C.

[1] S.I.Tatarinov, Abstr. 14th ILCC, Pisa, Italy, 1, 544 (1992).

INDUCTION OF SMECTIC A<sub>d</sub> PHASE IN BINARY MIXTURES COMPOSED OF COMPOUNDS WITH NEMATIC OR SMECTIC A<sub>1e</sub> PHASES, B.Ważyńska, Department of Material Sciences and Engineering Warsaw University of Technology, Narbutta 85, 02-524 Warsaw, Poland.

Two series of binary mixtures nBCB-nTPCHB and nCPB-nTPCHB were investigated. Compounds nBCB and nCPB with strongly polar -CN group form only the nematic phase for  $n \le 7$ . Compounds nTPCHB form the enhanced smectic  $A_1$  phase [1]. Phase diagrams of these mixtures were obtained by the thermomicroscopic method. A strong enhancement of the smectic phase region with simultanous appearance of the reentrant nematic phase on the phase diagrams is observed. The appearance of the reentrant nematic phase [2] as well as X-ray measurements confirm that the smectic  $A_d$  phase is formed in these binary mixtures. It was shown that the induction of the smectic  $A_d$  phase is a result of the existence of the virtual smectic  $A_d$  phase in the component with the strongly polar -CN terminal group. The length of the aliphatic chain of nBCB and nCPB components as well as of nTPCHB plays an important role in the induction of the smectic  $A_d$  and reentrant nematic phases.

1. R.Dabrowski, K.Czupryński, J.Przedmojski, B.Ważyńska, Liq.Cryst., 14, 1359 (1993).

2. B. Ważyńska, Liq. Cryst., 4, 399 (1989).

\*Supported by Polish Committee for Scientific Research (KBN), grant No 3T09B 193 08

C2P.22

BEYOND MEAN-FIELD: THE BLUE PHASES IN THE PRESENCE OF FLUCTUATIONS, Jochen Englert, Lech Longa\*, and <u>Hans-Rainer Trebin</u>, Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57/VI, D-70550 Stuttgart, Germany, \*Institute for Physics, Jagiellonian University, Reymonta 4, Kraków, Poland

Conventional mean-field theory renders the *structure* of the Blue Phases I and II correctly, but not their *position* in the temperature-chirality phase diagram. In particular it has not been managed so far to suppress the body centered cubic structure  $O^5$ . Using the concept of weak crystallization [1] we extend the Landau-Ginzburg-de Gennes free energy in a most natural way including order parameter fluctuations. Under consideration of one star of wave vectors it is shown that the formerly dominant  $O^5$  structure is destabilized.

Additionally we specify a modification of the fourth order Landau coefficient of the free energy accounting for nonlocal properties. Now the coefficient also depends on the quadrangle configuration of wave vectors. By again performing simple one star calculations we obtain a correct phase sequence, cholesteric —  $O^8(BP I)$  — isotropic, for a finite range of chirality, with  $O^5$  vanishing from the phase diagram.

[1] E.I. Kats, V.V. Lebedev and A.R. Muratov, Phys. Rep. 228, 1-91 (1993), and references therein

PHASE TRANSITIONS BY DILATOMETRY AND BIREFRINGENCE IN INTER-DIGITATED SMECTIC PHASES OF HIGHER HOMOLOGUES OF 50.m COMPOUNDS C.R. Prabhu, D.M. Potukuchi and V.G.K.M. Pisipati, Centre for Liquid Crystal Research and Education, Nagarjuna University, Nagajunagar 522510, India

C2P.23

The temperature variation of density (p) and refractive index anisotropy ( $\Delta n$ ) is studied weakly polar schiff based liquid crystalline higher homologues of N-(p-n-pentyloxy benzylidene )p-n-alkyl anilines, Viz; 50.m compounds with m = 14and 16 exhibiting [1] interdigitated smectic polymorphism. The observed density jumps (  $\Delta \rho/\rho X$  100 ) and the refractive index anisotropy An as a measure of orientational order parameter reflect the first order nature of isotropic to nematic (I-N ), nematic to interdigitated smectic-A (N-A<sub>d</sub>) transitions. The observed weakly first order nematic to interdigitated smectic-A transition is discussed in the light of McMillan theory and the recently reported results on the incommensurate smectic-A phases for the universality of the class. The density variation and the refractive index anisotropy show an anomalous behaviour accompanied with a non-linear dip immediately after N-A<sub>a</sub> transition reflecting the orientational disorder extended by increasing length of flexible end chain. A possible dipolar mechanism for the hitherto unobserved occurrence of smectic-A<sub>d</sub> phase (d < l) with the increasing length of end chain in these compounds is discussed

[1]. V.G.K.M.Pisipati and S.B.Rananavare, Liqd.Cryst., 13, 757, 1993.



THE PHYSICAL SENSE OF THE TEMPERATURE T\* SEPARATING CLASSICAL NE-MATIC AND QUASISMECTIC SUBPHASES IN 4,N-ALKYLOXYBENZOIC ACID, M. P. Petrov, Institute of Solid State Physics "G. Nadjakov", Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee blvd., 1784 Sofia, Bulgaria

The micro and macroscopical properties of the dimerized nematics with short range smectic order (4, n)-heptyl, octyl and nonyloxybenzoic acids - HOBA, OOBA and NOBA) are considered. The physical sense of the temperature T\*, where a drastic anomaly in the temperature dependence of typical liquid crystal constants starts, is discussed. On a microscopical level T\* is considered (using mid and far - IR spectroscopy) as a temperature in the middle of the nematic phase, where the mixture between cyclic dimers, open dimers and monomers undergous a sharp variation at cooling or heating. The monomers disappear below T\* and result a quasismectic state, while above this temperature a classical nematic establishs. On a macroscopical level the transition at T\*, indicated by microtextural, calorimetric analyses resembles an weak first order phase transition. The Landau - De Gennes theory describes the nematics assuming the molecules as rigid rods. The molecules of the dimerized nematics, however are very flexible. Therefore a theory of the nematics with internal degrees of freedom [1] can be applied in order to explain the physical nature of T\*.

[1] V.Pershin, V.Konoplev, Liq. Cryst., 12, 95 (1992).

## C2P.25

A CUSP CATASTROPHIC MODEL IN SMETIC LIQUID CRYSTALS PHASE TRANSITION, Dong He PEI, Xiang Tong LI, Wei Zhi SUN, Yasufumi IIMURA and Shunsuke KOBAYASHI, Division of Electronic and Information Engineering, Tokyo University of A&T, Koganei, Tokyo 184, JAPAN \*

In this research, we developed a catastrophe theory called a cusp model with the aim of analyzing phase transition in SmA-SmC phase transition. The potential function of the system is given by Landau free energy that consists of order parameter P, controllable parameter  $\alpha$  (containing temperature T, cell thickness d, and anchoring energy  $A_s$ ), and  $\beta$  (relating to temperature T and magnetic field H). Using there parameters we formulated a three dimensional catastrophic model, and we fund that there exist two stable region and one unstable region. When magnetic field, cell thickness, and anchoring energy remain constant, we obtained a phase transition of two dimensional phase, that is SmA-SmC phase transition. This result is in agreement with the result by C.C.Huang et al[Phys.Rev.Lett., 40, 1576(1982).]. From the phase transition between different phases in the three dimensional phase, it is obtained continuous, quasi-continuous, and cusp catastrophic discontinuous transition.

## C2P.26

PHYSICAL PROPERTIES OF THE MESOPHASES OF 4-n-HEPTYLOXY BENZYLIDENE -4'-AMINDAZOBENZENE (HBAAB), B. Adhikari, R.Paul and R.A. Vora, Department of Physics, University of North Bengal, Siliguri, 734430, India.

X-ray diffraction studies on the aligned sample of HBAAB in the nematic, smectic A and smectic B phases have been undertaken to determine the orientational order parameters (OOP's), correlation length, layer thickness and intermolecular distance as function of temperature. OOP values have been fitted satisfactorily with McMillan's theory with  $\alpha = 0.45$  and  $\delta = 0.595$ . OOP values, in the nematic phase, as determined from the refractive index measurements agree well with those obtained from x-ray studies. While both the N-Sm A and Sm A-Sm B phase transitions are found to be of the first order, the N-I phase transition appears to be weakly first order. Density and DSC studies confirms this trend.

\* M.S. University of Baroda, Vadodara, India. + C.S.I.R. Senior Research Fellow. P-150

INDUCTION OF A S<sub>B</sub> PHASE IN AN ISOTROPIC LIQUID BY SHEAR STRESS; EXTENSION OF CLAPEYRON'S EQUATION, R. Eidenschink, Nematel, Galileo-Galilei-Str. 10, D-55129 Mainz

The pressure induced formation of a high viscous  $S_B$  phase from a low viscous isotropic or nematic phase with promising aspects in tribolgy has been suggested some time ago[1]. Recently, very low coefficients of friction f were observed in slide bearings being operated in the region of mixed friction and lubricated with PCH derivatives[2]. According to the rules of lubrication[3] this can only be understood in terms of a highly viscous fluid being present. The distinct reduction of f was found at an operation temperature some 80 K above the transition temperature isotropic- $S_B$  at normal pressure. According to the equation of Clapeyron only a shift of some 20 K could be made explicable on the grounds of static pressure. It is shown that the change of shear stress, which depends on the change of viscosity during the phase transition, can yield a considerable effect on the transition temperature. Some experimental data backing the equation derived are presented.

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- [2] R. Eidenschink, A.M. Häger, Proc. 25th Freiburger Arbeitstagung Flüssigkristalle, Nr.21 (1996).
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C2P.28

INFRARED SPECTROSCOPIC CONFORMATIONAL INVESTIGATION OF A LIQUID CRYSTALLINE PHASE TRANSITION, C.S. DiGiacomo\* and J.L Koenig, Department of Macromolecular Science, Case Western Reserve University; R. Petschek, Department of Physics, Case Western Reserve University, Cleveland, OH, 44106, USA; M.A. Neubert, Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA.

A hemiphasmidic liquid crystal, 4-[3',4',5'-Tri(p-n-dodecyloxybenzoyloxy)benzoyloxy]4''-p-n-dodecyloxy-benzoyloxy-biphenyl<sup>1</sup>, exhibits two liquid crystalline mesophases with a transition between them at 71°C as confirmed by modulated DSC analysis. Fourier transform infrared spectroscopic analysis was performed using oriented samples of this liquid crystal prepared with rubbed polyimide plates. The analysis clearly shows a change at the the transition temperature in the conformation of the ether bonds located on the tetra-substituted benzene ring.

- Malthete et al, C.R. Acad. Sc. Paris, Series II, 303, 12, 1073 (1986); Bull. Soc. Chim. Fr., 131, 812 (1994).
- \*Supported through a grant from ALCOM.

C2P.29

EFFECTS OF REACTION EQUILIBRIA ON THE RE-ENTRANT NEMATIC AND SMECTIC-A POLYMORPHISM, A. Ferrarini, G.R. Luckhurst, P.L. Nordio\* and E. Spolaore, Department of Physical Chemistry, University of Padova, 2 via Loredan, 35131 Padova, Italy

The McMillan theory has been extended to take into account the presence of reaction equilibria involving the smectogenic species. Because of the molecular structures, which are characterized by high flexibility and, in many cases, by strong electric dipoles, two kinds of processes are expected to be of particular relevance: conformational transitions in the alkyl chains and association caused by dipolar interactions. Both situations have been treated by considering equilibria between two species, taken simply as uniaxial particles experiencing different potentials of mean torque and mean force. Under physically reasonable conditions re-entrant behaviour can result from the coupling between molecular order parameters and equilibrium constant. Thus, the phase sequence  $\operatorname{Sm}_{l}^{re}\operatorname{-N}^{re}\operatorname{-Sm}_{s}(N)\operatorname{-I}$ , where the indices l and s refer to the conformers with higher and lower tendency to orientational order, is predicted in the case of isomerization, while the sequence  $\operatorname{Sm}_{A_d}^{re}\operatorname{-N}^{re}\operatorname{-Sm}_{A_1}\operatorname{-(N)}\operatorname{-I}$  is predicted for systems of dimerizing molecules.

\* Human Capital Mobility Network Project N. 930282



MESOPHASES IN LONG-CHAIN ALKOXY ALCOHOL / ORTHOPHOSPHORIC ACID SYSTEMS, K. S. Krishnamurthy, and R. Balakrishnan, Applied Science Department, Faculty of Electrical and Mechanical Engineering, College of Military Engineering, pune, 411031, INDIA.

Mesophases in  $C_nH_{2n+1}O$   $C_mH_{2m}OH$  (n=16, m=4; n=18,20,m=2,3; n=22,m=3)/ aqueous  $H_3PO_4$  systems have been studied by optical and DSC methods. Upon cooling the isotropic liquid, the textural sequence commonly observed in these systems, over a wide concentration range, is: focal conics  $\rightarrow$  isotropic  $\rightarrow$  nematoids, myelin figures and oily streaks  $\rightarrow$  chevrons. The corresponding phase succession, being ascertained by SAXS measurements, is: hexagonal  $\rightarrow$  viscous isotropic  $\rightarrow$  lamellar  $\rightarrow$  gel. Particularly noteworthy is the striped chevron pattern of the low temperature phase developed in the homeotropic areas of the precursor phase. Similar textures are observed in the shubnikov-like smectic phases and in homeotropic smectics subject to mechanical tension. Here it is due to periodic structural undulations that corrugate a plane extraordinary wave passing through the sample. The undulations are possibly due to a mechanical tension arising from molecular chain elongation and stiffening.

The phase behaviour in title systems is compared with that in other amphiphile / H<sub>3</sub>PO<sub>4</sub> systems in which the mesophase structures have been categorised as thermotropic [1].

[1] M. Marthandappa, Nagappa, and K. M. Lokanath Rai, J. Phys. Chem. 95, 6369 (1991).

### C2P.31

UNUSUAL ISOSTRUCTURAL PHASE TRANSITIONS SEQUENCE UNDER EXTERNAL FIELD INFLUENCE, V. A. Konoplev, Vl. K. Pershin<sup>\*</sup>, R. A. Raevsky, D. E. Isaichenko, Theoretical Physics Department, Ural State Technical University, Ekaterinburg, 620002, RUSSIA.

The influence of an external orienting (magnetic or electric) field on successive phase transitions (PT) and multicritical phenomena is studied on the basis of the broaden version of the de Gennes model of smectic A (SmA) liquid crystal. A comprehensive topological classification of bifurcation sets (separatrices) and phase diagrams of mesophase is performed. It is described the effect of inducing of SmA-nematic tri-critical point which has been recently observed experimentally. The most unexpected case includes the existence of two different triple SmA<sub>1</sub> - SmA<sub>2</sub> - paranematic (pN) points on the phase diagram in the "temperature-field" coordinates. Thus, there is realized the following picture of the phenomenon: isostructural SmA<sub>1</sub> - SmA<sub>2</sub> PT taking place in the absence of the field is suppressed at the first triple SmA<sub>1</sub>-SmA<sub>2</sub>-pN point, above it the second order SmA<sub>1</sub>-pN PT is observed. Increasing of the external field induces the second triple SmA<sub>1</sub>-SmA<sub>2</sub>-pN point and an intermediate smectic phase which is eventually suppressed at the end critical point. Finally the only second order SmA<sub>1</sub> - pN phase transition is pertained.

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### C2P.32

MOLECULAR STRUCTURE IN VARIOUS PHASES OF COOLED LIQUID CRYSTALS. I.B. Estrela-Llopis, V.Ye. Pogorelov, Department of Physics, Kiev T. Shevchenko's University, Kiev, 252127. Ukraine

We have investigated the phase polymorphism of nematic MBBA by Raman spectroscopy. Regularities connecting parameters of vibrational bands with structural peculiarities of MBBA in different phases obtained at various rates of preliminary cooling of sample have been found. Using these connections the conformational angles, energetic barriers between different conformers, order of nonarrangement of various phases have been calculated. It has been these determined that initial nematic phase comprises three fractions of conformers and twist - angles values of the conformers and quantitative relationship between their fractions depends on thermal pre-history of sample. The dynamics and kinetics of phase transitions such as supercooled nematic -glass, glass - crystal and crystal-crystal has been investigated. The investigation of dynamics and kinetics of phase transitions which are accompanied by conformational conversations [1] have allowed to study their mechanism and to determine quantitative phase composition of complicated states obtained at different pre-history.

[1]. V.Ye. Pogorelov, I.B. Estrela-Llopis, Mol. Cryst. Liq. Cryst. 265, 237 (1995).

\* Supported by ISFound APS, Grant NUG39

SURFACE - INDUCED PRETRANSITIONAL ORDER IN THE ISOTROPIC PHASE NEAR THE ISOTROPIC - NEMATIC PHASE TRANSITION P. De Schrijver, W. Van Dael and J. Thoen, Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

We studied the formation of a nematic layer in the isotropic phase of the homologous series of alkylcyanobiphenyl liquid crystals (nCB, n = 5-12) near a polyamide-coated glass surface, using a transmission ellipsometric technique. The temperature dependence of the standard ellipsometric quantity  $\Delta$  is measured near the isotropic-nematic transition, using a high precision rotating analyser ellipsometer.  $\Delta$  is directly related to the residual birefringence at the walls. According to the theory of Tarczon and Miyano [1], who used the Landau - de Gennes theory to derive an analytic expression for the temperature-dependent birefringence,  $\Delta$  shows a logarithmic divergence at  $T_c$  (complete wetting) or remains finite (partial wetting), depending on the ratio of the order parameter at the wall  $S_a$  and the order parameter at the clearing temperature  $S_c = S(T_c)$ . In contrast to the results of Chen [2], who observed a wetting transition between 5CB and 6CB for nCB-DMOAP-glass systems, our results indicate that for the nCB-polyamide-glass configurations the wetting is always partial. For all samples the birefringence remains finite, resulting in a ratio  $S_c/S_c = 0.8$  for 5CB to 8CB. For 9CB the increase is even less ( $S_c/S_0 = 0.5$ ), while for 10CB to 12CB we measured no increase at all, probably as a consequence of non-uniform aligning of the samples.

[1] Tarczon J.C. and Miyano K., Chem. Phys. 73, 1994 (1980), [2] Chen W. et al., Phys. Rev. Lett. 62, 1860 (1989)

C2P.34

PHASE DIAGRAM, OPTICAL BIREFRINGENCE, DENSITY AND ORDER PARAMETER OF AN ESTER/CYCLOHEXANE MIXTURE SHOWING AN INJECTED SMECTIC PHASE, M.K. Das and R. Paul, Department of Physics, North Bengal University, Siliguri, Darjeeling, Pin-734430, W.B., India.

The phase diagram, refractive indices  $(n_0,n_e)$ , densities  $(\rho)$  and orientational order parameter (<P2>) of the binary mixtures of p-cyanobiphenyl trans-4-pentyl cyclohexane carboxylate (CPPCC) and 4-n-hexyl phenyl 4-n' pentyloxy benzoate (ME5O.6) exhibiting an injected smectic phase have been studied. The mixture shows an injected smectic phase in the range 0.05 < x < 0.53, where x is the mole fraction of CPPCC. Maximum stability of smectic phase occurs for mixture having x=0.25. The physical parameters  $n_0,n_e$ ,  $\Delta n$  (=  $n_e$ - $n_0$ ),  $\rho$  and <P2> at T= 35°C in the smectic phase and  $n_{iso}$ , the isotropic refractive index show definite minima near x=0.37. The thermal expansion coefficient bs in the smectic phase has also a flat maximum near x=0.25. Change in  $\Delta n$  and <P2> at the smectic-nematic transition show a prominent maximum near x=0.2.

C2P.35

ANCHORING TRANSITIONS AND CRITICAL POINTS IN PHASE DIAGRAM OF NEMATIC LIQUID CRYSTAL ON MUSCOVITE SUBSTRATE, <u>B. M. Borovik</u>, V. A. Konoplev, and Vl. K. Pershin<sup>\*</sup>, Theoretical Physics Department, Ural State Technical University, Ekaterinburg, 620002, RUSSIA.

By adsorbing a thin nematic layer onto muscovite mica substrate, Bechhoefer et al [1] have observed variations in liquid crystal orientation with relative humidity. The aim of the present paper is a rigorous analysis of the Bechhoefer potential on the basis of applied catastrophe theory techniques. The results are as follows: i) the occurrence of tri-critical point dividing the coexisting line of  $\theta=0^{\circ}$  ( $\theta$  is the angle of molecular orientation with respect to some fixed crystallographic axes of the substrate) and bistable anchoring phases into first—and second—order parts is predicted; ii) the fundamentally different dependencies simulating the relationship between the  $\theta$  angle and the external parameters (humidity, temperature) are recognized; iii) the point with coordinates (3, 0) occurs in the  $\{a, b\}$  phase diagram at which monotonicity and convexity of curves  $\theta=\theta(b)$  change (a, b) are the Bechhoefer model parameters).

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\*Supported by RFFI Grant No 95-02-04783



PHASE BEHAVIOR OF NEMATIC-NONNEMATIC BINARY SYSTEMS — EFFECTS OF HYDROGEN BONDING —, S. Yoshida, T.Narui, K.Asaba, J.Kawata and S.Kobinata, Department of Materials Science and Technology, Toin University of Yokohama, 1614 Kurogane-cho, Midori-ku, Yokohama, 227, JAPAN

The addition of non-nematic solute to a nematic liquid crystal usually causes the depression of the nematic-isotropic phase transition temperature and the appearance of two-phase region( $T_N,T_I$ ). Only a few unusual nematic-nonnematic binary systems are known to exist in which the addition of non-nematic solute cause the increase in  $T_{NI}$ . We studied effects of the addition of various solutes on n,n'-pentyl cyano biphenyl(5CB), and found that many solutes which possess the ability of hydrogen bonding with 5CB, such as p-carboxylic biphenyl and p-phenyl phenol, can increase the nematic-isotropic phase transition temperature. The addition of p-carboxylic biphenyl shows not only remarkable increase in  $T_N$  and  $T_I$ , but also curious phase behavior prior to  $T_N$ . The solutes with various functional groups (-COOH, -OH, -NH<sub>2</sub>) at various positions were studied to clarify the effect of H bonding on the phase behavior of nematic-nonnematic system.

#### C2P.37

CRITICAL SOUND DAMPING: WHEN DOES SCALING HOLD? <u>L.G. Benguigui</u>\*, D. Collin and P. Martinoty, Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, U.R.A. au C.N.R.S. n°851, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France.

The dynamic specific-heat theory is used to show that the dynamic scaling-laws deduced from mode-mode coupling for ultrasound damping are never rigorously verified. In the case of the N-SmA transition, departure from these laws is too slight to be observed for compounds with a 3DXY-type  $\alpha$  exponent and a  $|A|/C_0$  ( $C_1 = C_0 + At^{-\alpha}$ ) ratio of less than 0.5, but it must be fully visible for compounds with a  $|A|/C_0$  ratio of  $\sim 1$ . A marked departure should also appear for compounds whose N-SmA transition is in the vicinity of a tricritical point.

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#### C2P.38

HIGH-RESOLUTION CALORIMETRIC INVESTIGATIONS OF SEVERAL PERFLUORINATED LIQUID-CRYSTAL COMPOUNDS, \* M. Veum, and C. C. Huang, Department of Physics, University of Minnesota, Mpls., MN 55455, USA

In light of several unique physical properties being previously discovered in one of the partially perfluorinated liquid crystal compounds [1], we have started our experimental investigations of another homologous series of partially perfluorinated liquid-crystal compounds which exhibits the smectic-A-smectic-C transition. Our results clearly demonstrate that this new group of liquid crystal compounds exhibits a very different temperature dependence of heat capacity near the smectic-A-smectic-C transition. We will report our findings.

[1] T. Stoebe, et al., Phys., Rev. Lett. 73, 1384 (1994); L. Reed, et al., Phys. Rev. E 52, R2157 (1995), T. Stoebe, Phys. Rev. E, accepted for publication.

\* Supported in part by NSF Grant DMR 93-00781.

PHASE BEHAVIOR OF FD VIRUS PARICLES AND POLYSTYRENE LATEX SPHERES, M. Adams, S. Fraden, Department of Physics, Brandeis University, Waltham, MA. 02254, USA.

We have investigated the phase diagram of the 1 micron long rod-like fd virus and colloidal spheres (polystyrene latex). We have explored concentration ranges for both components, and varied the sphere diameter. The system exhibits depletion flocculation and shows liquid crystalline ordering of the rods. We found that for large rod/sphere size ratios, a liquid-liquid phase separation occurred and for small rod/sphere size ratios, a liquid-solid phase separation occurred. These findings agree with predictions of prior simulations and experiments [1]. However, for intermediate sphere diameters, a novel behavior was observed. Mixtures of fd with spherical colloid of diameter approximately equal to .1 microns exhibited columnar and lamellar structures, similar to lyotropic liquid crystal phases. We present our observations of this rod/sphere system and compare our findings with previous experiments.

[1] E.J. Meijer and D. Frenkel, J. Chem. Phys. 100 (9), 6873 (1994).

C2P.40

ANOMALOUS PHASE TRANSITION IN DIPALMITOYLPHOSPHATIDYLETHANOL AMINE - PALMITOYLPHOSPHATIDYLCHOLINE-WATER SYSTEM, <u>A.Checchetti</u><sup>1</sup>, G.Chidichimo<sup>1</sup>, .A.Golemme<sup>1</sup>, D.Grasso<sup>2</sup>, D.Imbardelli<sup>1</sup>, C.La Rosa<sup>2</sup>, F.P.Nicoletta<sup>1</sup> and P. Westerman<sup>3</sup>, <sup>1</sup>Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy; <sup>2</sup>Dipartimento di Chimica, Università di Catania, via A. Doria 8, 95125 Catania, Italy; <sup>3</sup>Department of Biochemistry and Molecular Pathology, Northeastern Ohio Universities' College of Medicine, P.O. Box 95, Rootsown, Ohio 44272, U.S.A.

A second order phase transition at 62.5 °C for an equimolar mixture of 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine and 1-palmitoyl-sn-glycero-3-phosphocholine in water (34 weight %) has been demonstrated by differential scanning calorimetry, scanning dilatometry, isotermal compressibility measurements. This transition occurs 15 °C above a first order transition observed in the same system. <sup>31</sup>P and <sup>2</sup>H nuclear magnetic resonance results are consistent with the presence of a defective bilayer in the temperature range between the first and second order transitions. In the defective bilayer it is proposed that conically shaped PLPC molecules prefer regions with high curvature while DPPE molecules are mostly confined to flat regions of the bilayer. Several possible molecular models are described. Both below the first order transition, and above the second order transition the molecular assemblages exist as lamellar bilayers.

C2P.41

MODEL OF LAYER-BY-LAYER THINNING TRANSITION IN THIN FILMS, T. Kranjc and S. Žumer, Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

Free-standing smectic liquid-crystal films exhibiting the interesting phenomenon of layer-by-layer thinning transition are studied where, instead of abrupt rupture of the film at or below Sm-A-isotropic transition temperature  $T_c$ , discrete jumps in film thickness are observed when temperature is increased, and the film eventually breaks at a temperature above the bulk value  $T_c$  [1]. Starting with a molecular pair interaction potential of a McMillan form and deriving a single effective potential along standard lines, the behavior of thin films with changing temperature is studied which, depending on parameters of the potential, may or may not exhibit the phenomenon of layer-by-layer thinning transition. Fluctuation profile of the order parameters within smectic layers of the film is considered and the relevance of fluctuations for the jumpwise thinning process is discussed.

[1] T. Stoebe, P. Mach, and C.C. Huang, Phys. Rev. Lett. 73, 1384 (1994)



CONFINEMENT EFFECTS AT THE NEMATIC TO ISOTROPIC TRANSITION OF 5CB, S. Qian, D. Finotello\*, Department of Physics and Liquid Crystal Institute, Kent, OH 44240, USA.

The NI transition of 5CB in bulk and confined to Millipore filters and Anopore membranes is investigated by using a high resolution ac calorimetry. Millipore filters have a geometry of interconnected irregular voids with an average void size  $\sim 0.2~\mu m$ , while Anopore membranes possess a well defined geometry: uniformly distributed parallel cylindrical pores of diameter  $\sim 0.2~\mu m$ . Although the transition temperature shifts downward in both confining substrates, it is due to distinct mechanisms. In the axial Anopore confinement, elastic distortions dominate the shift of  $T_{NI}$  [1]. In Millipore, the cause could be a combination of the elastic constraints and random field effects. Critical behavior is also altered by the confinements: the heat capacity exponent  $\alpha$  is driven away from the bulk value.

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\* Supported by NSF Grant DMR 89-20147.

# C2P.43

IMPROVED ANALYSIS OF DYNAMICS IN LIQUID CRYSTALS BY ANGULAR DEPENDENT FIELD CYCLING STUDIES, J. Struppe, and F. Noack, Physikalisches Institut, Universität Stuttgart, 70550 Stuttgart, Germany

The analysis of molecular motions in liquid crystals, namely of collective motions, self-diffusion and molecular rotations, which affect the <sup>1</sup>H spin relaxation time  $T_1$  can be performed in more detail by measuring both the Larmor frequency and angular dependence  $T_1(\nu,\beta)$  with an improved field-cycling technique [1]. This is done by cycling both the strength and orientation of the field. Such studies were made on the nematic liquid crystal 5CB. For frequencies larger than 10 MHz we used 5CB samples which were oriented mechanically by confinement effects in the cylindrical pores of anopore membranes. We found that the collective motions reveal the expected angular dependence and that the rotation contributions allow to contrast different rotational diffusion models. In the local field region  $\nu \leq 10$  kHz a deep  $T_1(\nu,\beta=90^\circ)$  minimum indicates that the familiar relaxation expressions [2] are not valid.

[1] J. Struppe and F. Noack, Liquid Crystals (1996), in press;

[2] R. Y. Dong, Nuclear Magnetic Resonance of Liquid Crystals, Springer, Heidelberg (1994).

#### C2P.44

FLUCTUATIONS OF TENSOR ORDER PARAMETER IN PARANEMATIC BOUND-ARY LAYER P. Ziherl and S. Žumer, Dept. of Physics, University of Ljubljana, Jadranska 19, 1111 Ljubljana, Slovenia

Above  $T_{NI}$ , the behavior of liquid crystals confined by porous materials is characterized by the surface-induced parameterion [1]. In order to broaden the understanding of these systems, the fluctuations of tensor order parameter in partially ordered layer are studied within the framework of Landau-de Gennes theory [2]. In the boundary-layer phase with strong parametric order, the lowest longitudinal mode (nematic order parameter mode) turns out to be significantly slower than in both nematic and weak paramematic phase. Immediately above the critical temperature, the four transverse modes (biaxiality and quasidirector modes) may be divided into two classes: the slow ones are localized in the center of the layer, where the degree of order is lowest, whereas the fast ones penetrate into the partially ordered boundary layer.

- [1] P. Sheng, Phys. Rev. A 26, 1610 (1982); G. S. Iannacchione et al., Phys. Rev. Lett. 71, 2595 (1993).
- [2] A. Sonnet et al., Phys. Rev. E 52, 718 (1995).

NMR AND DIELECTRIC STUDIES OF NANO-CONFINED NEMATOGENS,

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Confinement of a nematogen in submicrometer cavities can produce substancial effects on the nematic-isotropic phase transition and on order and orientation of the nematic phase. The system investigated is nematic 5CB confined in random cavities of controlled porous glass (Geltech Inc.) with spezific pore sizes (2.5 nm, 5.0 nm, and 7.5 nm resp.) and narrow pore size distribution. We probe the liquid crystalline order and molecular mobility by means of <sup>13</sup>C NMR and broadband dielectric spectroscopy.

A mathematical model is introduced which describes the combined influences of orientational order and diffusional averaging in randomly oriented pores on NMR spectra. The fit of computed line shapes to experimental spectra yields order parameters and information on molecular self-diffusion.

Broadband dielectric spectra clearly indicate the co-existence of a rigidly bound surface layer of 5CB at the pore walls and a free pore volume with a molecular mobility comparable to the bulk phase. Exchange rates between the surface and free molecules can be extracted from the experimental data.

In all samples, the existence of a nematic range is veryfied. Isotropic-nematic transition and crystallization temperatures of the confined nematogen are considerably suppressed with respect to the bulk phase.

C2P.46

THE CHOLESTERIC-NEMATIC TRANSITION IN SPHERICAL DROPLETS SUBJECTED TO ELECTRIC FIELDS, R.R. Swisher and P.P. Crooker, Department of Physics and Astronomy, University of Hawaii, 2505 Correa Road, Honolulu, HI USA

The behavior of the field-induced cholesteric-nematic transition is strongly modified when performed in confined systems. We have studied this transition in spherical droplets subjected to electric fields using polarized microscopy in which the droplet is viewed both parallel to and perpendicular to the field. At zero field, the droplet takes on the Frank-Pryce texture with a non-singular radial x-disclination and equi-twist surfaces appearing as spirals when viewing along the field. As the field increases, the spirals unwind, both from the center and from the droplet surface, until at the highest fields a single twist wall remains. The evolution of the Frank-Pryce defects is discussed and the behavior of the pitch with electric field is compared to the bulk case.

C2P.47

ELLIPSOMETRY AT THE NEMATIC - ISOTROPIC PHASE TRANSITION IN CONFINED GEOMETRIES\*; <u>Karl A. Crandall</u> and Charles Rosenblatt, Dept. of Physics, Case Western Reserve Univ., Cleveland, Ohio 44106, USA; and Fouad M. Aliev, Dept. of Physics and Materials Research Center, University of Puerto Rico, San Juan, P.R. 00931 USA

Small, parallel, cylindrical pores in a thin polymer film were impregnated with the liquid crystal pentylcyanobiphenyl. Optical retardation measurements, performed around the bulk nematic-isotropic phase transition temperature, are reported [1]. Relative to the bulk, a depression  $\Delta T_{NI}$  of the phase transition temperature region was observed, although for the smallest diameter pores (d=150 Å),  $\Delta T_{NI}$  was found to be larger than expected. The profile of the optical retardation vs. temperature was also found to be anomalously sharp for the d=150 Å pores. The results are discussed in terms of current models.

[1] K.A. Crandall, C. Rosenblatt, and F.M. Aliev, Phys. Rev. E 53, 636 (1996)

<sup>\*</sup> Supported by the NSF under grant DMR-9502825 and by DOE-EPSCoR under grant DE-FG02-94ER75764



COMPUTER SIMULATIONS OF LIQUID CRYSTAL ORDERING IN AEROGELS T. Bellini<sup>1</sup>, C. Chiccoli<sup>2</sup>, P. Pasini<sup>2</sup>, C. Zannoni<sup>1</sup>, <sup>1</sup> Dip. di Elettronica dll' Università,27100 Pavia, Italy - <sup>2</sup> INFN, Sezione di Bologna, 40126 Bologna, Italy - <sup>3</sup>Dip. di Chimica Fisica ed Inorganica dell'Università, 40136 Bologna, Italy

We have performed Monte Carlo simulations of droplets with various types of boundary conditions in order to check if the independent pore model of liquid crystals in silica aerogel systems is appropriate or not. Our results indicate that the most straightforward simplification of the silica aerogel structure, i.e. that of independent pores with 3D random boundary conditions, reproduces qualitatively the features observed in real experiments. However, it cannot reproduce both calorimetric and turbidity data at the same time. This fact suggests the need of going beyond the independent pore approximation. Comparisons with other simulation models are also performed.

# C2P.49

TIME PARAMETERS OF CHOLESTERIC-NEMATIC PHASE TRANSITION AND THEIR INFLUENCE ON WORKING CHARACTERISTICS OF LIGHT MODULATORS, L. Vernikova, J. Semenova, O. Nevmerzhitska, D. Badbayar, State University "Lvivska Politechnika", Bandera Str., 12, Lviv, Ukraine, 290646.

studies time parameters This work is dedicated to Of transition in nematic-cholesteric nematic phase nematic mixtures on the base of strong and weak polar prystals with dopants of cholesterine esters with aim to determine radiation modulators parameters. their influence on laser comparative analysis of theoretical models with experimental data time cholesteric-nematic phase transition was carried out for control pulse parameters parameters. The recommendations for optimization in order to improvement of modulation characteristics of laser radiation modulators were elaborated.

#### C2P.50

ELECTRIC FIELD EFFECT ON THE NEMATIC-ISOTROPIC PHASE TRANSITION FOR LIQUID CRYSTALLINE POLIMERS HAVING MESOGENIC GROUPS IN THE SIDE CHAIN, T.A. Rotinyan, S.G.Kostromin, V.P. Shibaev, Department of Physics, St. Petersburg State University, St.Peterburg 198904, Chemistry Department, Moscow State University, Moscow, 119899, Russia.

Pulsed electric fields are used to study the influence of a srtong field on the nematic-isotropic phase transition for termotropic LC comb-like polyacrylic polymer having cyanobyphenyl groups in side chains. The electric field-induced optical anisotropy is observed and it is shown that such electric fields can shift the transition temperature substantially. The induced birefringence in the isotropic phase and the shift of the transition temperature are measured as a function of the electric field strength. The results are compared with the results for its low-molecular analogs [1].

[1] Rotinyan T.A., Rjumtsev E.I., and al., 1987, Soviet Phys. JETP Lett., 46,331.

DISCOID NEMATICS: ORIENTATIONAL ORDER, PHASE TRANSITIONS AND CRITICAL BEHAVIOR, E.M. Averyanov, Institute of Physics, Krasnoyarsk, 660036, RUSSIA

New experimental data on the orientational order of the molecules in the thermodynamically stable, metastable and reentrant phases of discoid nematics  $N_D$  belonging to various chemical classes and homologues has been presented [1]. The order parameter S(T) in the stable and metastable phases  $N_D$  is described quantitatively by the Landau - de Gennes theory. The  $N_D$ -I transition is simultaneously close to an isolated Landau critical point and to the tricritical point. The  $N_D$ - $D_{hd}$  transition is found to be strong transition of the first order with the jump  $\Delta$  S=0.1-0.2 and unexpectedly strong relation between orientational and two-dimensional translational molecular ordering. The bare correlation length  $\xi_0$  of fluctuations in S is argued to be larger by several times than that one for the thermotropic calamite nematics. The proper and effective exponents characterising the temperature behavior of S as well as the nematic susceptibilities of the first and second order have been obtained and discussed. The conformational state of the flexible molecular chains in the reentrant  $N_D$  phase has been found to depend on their length and the decrease in the molecular polarizability anisotropy has been observed as a result of elongation of the chains withing the homologous serie.

[1] E.M. Averyanov, JETP Lett., 61, 815 (1995); 63, N1 (1996); Crystallogr. Rep., in press (1996).

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FERROELECTRIC AND ELECTROCLINIC POLARIZATION CLOSE TO THE SMECTIC C\* - A\* TRANSITION, F. Gießelmann, A. Heimann, and P. Zugenmaier, Institute of Physical Chemistry, TU Clausthal, D-38678 Clausthal-Zellerfeld, Germany, <u>D. Hermann</u>, L. Komitov, B. Stebler, and S. T. Lagerwall, Physics Department, Chalmers University of Technology, S-41296 Göteborg, Sweden

Polarization properties of ferroelectric liquid crystals are widely investigated by the triangle wave technique which was recently criticized concerning its interpretation close to the SmC\* - SmA\* transition [1]. The tilt angle and the total polarization (dielectric, electroclinic, and spontaneous polarization) of a high- $P_s$  FLC (W316) was measured in the vicinity of the phase transition as function of the electric field strength applied. In order to obtain true values for the spontaneous polarization  $P_s$ , the data are analyzed and extrapolated to zero electric field by application of the generalized Landau-expansion. The results are compared to  $P_s$ -values obtained from the triangle wave technique and large differences up to 50 % are observed. These deviations are explained by the non-linearity of the electroclinic effect close to the SmC\* - SmA\* transition which contributes to the polarization reversal peak and falsifies the spontaneous polarization evaluated from the triangle wave technique.

[1] J. Ruth, J. V. Selinger, and R. Shashidar, Appl. Phys. Lett. 65, 1590 (1994)

D1P.02

CHANGES IN IR TRANSITION MOMENT DIRECTION OF HYDROGEN-BONDED CARBONYLS IN FERROELECTRIC LIQUID CRYSTALS, W. G. Jang, C. S. Park, K. H. Kim, J. E. Maclennan, Noel A. Clark, Department of Physics, and D. Walba, Department of Chemistry, University of Colorado, Boulder, CO, 80309, USA

Polarized FT-IR spectroscopy has been applied to investigate the polarization direction change due to hydrogen bonding in liquid crystal phases. Generally, the polar absorption profile of C=O stretching has a maximum for incident light with polarization perpendicular to the layer normal in smectic A phase as expected for a 60° transition moment direction from molecular long axis. However, due to hydrogen-bonded interactions, for example as found in C=O---H-O and C=O---H-N, not only is the maximum peak position of C=O changed to the layer normal direction but also the dichroic ratio is changed. These results can be interpreted by conformational change and transition moment direction calculations using ab initio electronic structure methods.

\*Supported by NSF MRG Grant DMR 92-24168

D1P.03

DIRECT EVIDENCE OF ZIG-ZAG SHAPE OF LIQUID CRYSTAL MOLECULAR STRUCTURE IN CHIRAL Smc PHASE USING POLARIZED FTIR SPECTROSCOPY, C. S. Park, W. G. Jang, K. H. Kim, and Noel A. Clark, Department of Physics, University of Colorado, Boulder, CO, 80309, USA

We report direct evidence for zig-zag molecular shape in the chiral Sm C phase by Fourier Transform Infrared Spectroscopy(FTIR). Polar plots of the absorption profiles of phenyl groups and alkyl tails in the chiral SmC phase clearly show that W399 and W314 have structures in which the tails tilt 100 degrees less than the cores do from the layer normal at temperatures far below the SmA to SmC phase transition. The behaviors of the phenyl core, alkyl tail and optical tilts from the layer normal vs. temperature will be presented. In general the materials studied the orientation difference between core and tail is less than 2 degrees. X-ray measurement of layer spacing and time resolved IR spectroscopy results will be discussed.

\*Supported by NSF MRG Grant DMR 92-24168



THE GIANT SURFACE ELECTROCLINIC EFFECT IN A CHIRAL SMECTIC A, Renfan Shao, Noel A. Clark, Joseph E. Maclennan, Department of Physics, University of Colorado, Boulder, CO 80309, USA; Daniel J. Dyer, David M. Walba, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309, USA

We report the observation of a very large surface electroclinic effect in the smectic A (SA) phase of the chiral compound W415. This compound has an isotropic - SA - SC - X phase sequene and in a pure enantiomer the angle between the rubbing direction and the layer normal is 24° when the SA phase grows in planar alignment. The sign of this surface electroclinic tilt depends on the molecular handeduess and is zero for the racemic mixture, increasing linearly with enantiomeric excess and saturating for ee near 1. The layer structure and defect of cells made from this material will be discussed.

\* Supported by NSF MRG GRANT DMR 9224168 and ARO GRANT DAAH-04-93-G-0164

# D1P.05

LINEAR ELECTROOPTIC EFFECT IN A CHIRAL SM C\* LIQUID CRYSTAL: DYNAMICS OF HELIX DEFORMATION\*, Erik Kangas, <u>Jian-feng Li</u>, and Charles Rosenblatt<sup>‡</sup>, Physics Dept., Case Western Reserve Univ., Cleveland, Ohio 44106 USA

Measurements are reported for the optical response in the classical electroclinic geometry of a chiral smectic C\* liquid crystal [1]. The sample was subjected to a weak a.c. electric field applied perpendicular to the helical axis. The response was found to be linear in field for E much smaller than the critical field associated with complete unwinding, and nearly independent of sample thickness, falling off approximately as  $f^{-1}$  in the frequency range 200 < f < 20~000 Hz. The behavior is modeled by a time-dependent Landau-Ginzburg model in which both the local polarization and dielectric anisotropy are coupled to the electric field.

- [1] E. Kangas, J.-F. Li, and C. Rosenblatt, Phys. Rev. E 53, 696 (1996)
- \* Supported by the NSF under grant DMR-9502825
- ‡ E-mail address: cxr@po.cwru.edu

#### D1P.06

SPONTANEOUS POLARIZATION IN TILTED SMECTICS, Demitri J. Photinos and Andreas F. Terzis, Department of Physics, University of Patras, Patras 26100, Greece and Edward T. Samulski, <u>Theo J. Dingemans</u>, Aidi Chen, and Chi-Duen Poon, Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill North Carolina 27599-3290

The rapid electro-optic response of ferroelectric liquid crystals (FLCs)—spontaneously polar phases—makes them candidates for the next generation of liquid crystal displays and a considerable effort has been underway to establish design rules for synthesizing more responsive materials. Herein we describe the key features of a simple theory [1] which suggests that polarity is indigenous to tilted smectics and not a consequence of mesogen electrostatic attributes, e.g. dipole moment and/or molecular chirality. We suggest classes of prototypical FLCs and NMR experiments which could critically test the theory.

[1] D.J. Photinos and E.T. Samulski, Science, 270, 783 (1995).

AN UNIQUE ALKYL CHAIN BEHAVIOUR IN LOW MOLAR MASS FERROELECTRIC LIQUID CRYSTAL SHOWED BY POLARIZED INFRARED SPECTROSCOPY. <u>T.S. Perova</u><sup>1</sup>, and J.K.Vij<sup>2</sup>, <sup>1</sup> Vavilov State Optical Institute, St.-Petersburg, 199034, RUSSIA; <sup>2</sup>EEE Department, Trinity College, Dublin-2, IRELAND.

Fourier transform infrared spectra of a ferroelectric liquid-crystalline material: 4-(3)-(S)-methyl-2-(S)-chloropentanoyloxy-4'-octyloxy-biphenyl has been investigated at different temperatures and as a function of polarizer rotation angle, polarity and magnitude of the aplied electric field in its SmC\* phase. The analysis of the C=O stretching vibration suggests the existence of three possible conformations for the ester groups of the FLC molecule; the relative populations of which may vary significantly as a function of temperature. One of the conformer exists primarily in the crystalline state, the other one exists primarily in the SmA and the isotropic phase. The relative populations of these two conformations are approximately equal in the SmC\* phase. These observed conformations correspond to different angles of the C=O bond with respect to the benzene ring. The analysis of peak intensity behaviour on polarizer rotation angle strongly shows that there is a preferable orientation for the C=O bond with respect to the mesogenic group in SmC\*.phase. It means that for this particular FLC molecule (with a short alkyl chain, containing 2 chiral groups: C-Cl and C-CH<sub>3</sub>, from one side of molecule) the rotation of alkyl chain is restricted. The unique behaviour of two different C-CH<sub>3</sub> groups in this alkyl chain, found for the first time, strongly supports this conclusion.

D1P.08

QUANTITATIVE CALCULATION OF SPONTANEOUS POLARIZATION IN FLCS\*, <u>D.J. Photinos\*</u>, E.T. Samulski\*, A.F. Terzis\*, \*Department of Physics, University of Patras, Patras, 26110 Greece, \*Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA.

A recently proposed theory[1] suggests that polarity is indigenous to tilted smectic and not a consequence of molecular chirality or of electric dipole interactions. To critically test this theory we study a class of ferroelectric liquid crystals which exhibit varying polarization within a minimally varying mesogen structure. We evaluate the first and second rank order parameters of the members of this series taking into account the details of molecular structure and conformation. The results compare favorably with available experimental values of spontaneous polarizations and of bond order parameters obtained from NMR measurements on these compounds[2].

[1] D.J. Photinos, and E.T. Samulski, Science, 270, 783 (1995).

[2] C.D. Poon and B.M. Fung, J. Chem. Phys., 91, 7392 (1989).

D1P.09

SYNTHESIS AND CHARACTERISATION OF NOVEL FERROELECTRIC LIQUID CRYSTALS OF TYROSINE DERIVATIVES

P.Anjana Kumar, P.S.S.J. Sastry, D.M. Potukuchi and V.G.K.M. Pisipati, Centre for Liquid Crystal Research and Education, Nagarjuna University, Nagarjunanagar 522 510. India. Novel series of ferroelectric liquid crystals derived from an α-chloro amino acid, viz., (4S-)N{4-(4'-alkyloxy)-2-chloro phenyl alkoxy)benzyloxy)2-hydroxy benzylidene}4-alkyl anilines with the structural formula,

$$RO \stackrel{\circ}{\bigcirc} CH_2 \stackrel{\circ}{C}HCO \stackrel{\circ}{\bigcirc} CH = N \stackrel{\circ}{\bigcirc} R'$$

abbreviated as  $nT^*(OH)m$ , where n=4 to 12 and m=4 to 16 are synthesised. The chiral centre in the  $\alpha$ -position of the amino acid is induced [1] by the nucleophilic substitution of  $-NH_2$  group by a -Cl atom through a diazonium salt. The  $nT^*(OH)m$  liquid crystal compounds are found to exhibit a phase sequence variant i.e., smectic-A, -C\*, -I\*, -F\* and smectic-G phases with the characteristic microscopic textures under crossed polars.

[1]. S.C.J.Fu, S.M.Birnbaum and I.P.Greenstein, J.Amer.Chem.Soc., 76, 6054 (1954)

<sup>\*</sup> Work suported by the NSF Grant DMR-9412701.

# D1P

# D1P.10

LOW FREQUENCY DIELECTRIC RESPONSE IN THE SMECTIC C' PHASE OF A FLC MIXTURE, S. Sinha Roy, T. Pal Majumder and S. K. Roy, Dept. of Spectroscopy, I.A.C.S., Jadavpur, Calcutta - 32, India.

Experimental studies of the dielectric response of a ferroelectric liquid crystal ( FLC ) mixture having low spontaneous polarization at different temperature and frequency have been done in smectic  $C^{\bullet}$  ( Sm- $C^{\bullet}$ ) phase. The dielectric measurements were carried out on homogeneously aligned samples. In the Sm- $C^{\bullet}$  phase the temperature dependence of the dielectric contribution in the Goldstone mode has been measured using two cells of thickness of 17  $\mu m$  and 100  $\mu m$ . Dielectric strength and the corresponding relaxation frequency are determined. From the experimental results it has been observed that the nature of variation of the curves of dielectric strength and relaxation fgrequency with temperature are similar for the two cells, but the dielectric strength obtained for the 17  $\mu m$  cell is higher than that obtained for 100  $\mu m$  cell at all temperatures. On the other hand the temperature dependence of the relaxation frequency for both cells is almost the same. The Goldstone mode rotational viscosity has been calcutated using evaluation model from the dielectric results. The experimental results have been discussed and compared with the theoretical results.

# **D1P.11**

COVARIANT ELASTICITY THEORY FOR THE SMECTIC C\* PHASE, Yashodhan Hatwalne<sup>†</sup>, Sreejith Sukumaran<sup>†</sup> and <u>P.B. Sunil Kumar</u><sup>‡</sup>, <sup>†</sup>Raman Research Institute, Bangalore 560 080. India. <sup>‡</sup>Institute for Mathematical Sciences, Madras 600 113, India.

We set up the covariant elasticity theory for the smectic C\* phase. This theory includes the gauge term -as in de Gennes theory for smectic A-whereby Type I and Type II smectic C\* phases are clearly defined. Since we define the c director to be always lying on the plane of the layers, this theory is also suited to analyze problems where the layers are not asymptotically flat.

#### D1P.12

CHROMATIC PROPERTIES OF DYE GUEST - HOST FERROELECTRIC LIQUID CRYSTALS, O-Chou Kao, <u>Jiunn-Yih Lee</u>, Department of Textile and Polymer Engineering, National Taiwan Institute of Technology, 43, Keelung Road, Section 4, Taipei, Taiwan, Republic of China.

A single polarizer of Dye Guest-Host Ferroelectric Liquid Crystals (DGHFLC) and its operational procdure were described. The electrooptical and chromatic properties of a FLC, doped with two dichroic dyes in black and red coloration were studied. From the results, it is indicated that with increasing of dye concentration, the contrast ratio, color difference  $\Delta E^*$  and chroma  $C_{uv}^*$  of the DGHFLC cell can be improvement. However the lightness  $L^*$  decreases.

Hence,the off (coloured) state and the on (colourless) state of cell under applied electric field on the chromaticity diagram can be located. In the case of DGHFLC cell the color difference  $\Delta E^*$  and contrast ratio continuous to increase with increasing voltage after almost saturated. The threshold voltage of DGHFLC cell remains the same as the FLC host. The response time of the DGHFLC cell increases due to the increase in rotational viscosity of the FLC host. The increasing behavior in rotational viscosity leads to excellent bistable state and a good memory effect.

VISCOSITY MEASUREMENT OF FERROELECTRIC LIQUID CRYSTALS USING A SHEAR HORIZONTAL MODE DEVICE, <u>H. Moritake</u>, K. Takahashi, K. Yoshino\* and K. Toda, Department of Electronic Engineering, The National Defense Academy, Hashirimizu, Yokosuka 239, JAPAN, \*Faculty of Engineering, Osaka University, Yamada-Oka, Suita, Osaka 565, JAPAN.

Viscosity measurement of ferroelectric liquid crystals (FLCs) has been performed using a shear horizontal (SH) mode device which has two acoustic wave channels. The FLC cell is mounted on one channel and the other channel is used as a reference. The upper substrate of the FLC cell is a glass plate coated with polyimide which is rubbed to achieve unidirectional homogeneous alignment. The acoustic phase delay difference between two output signals propagating the channels has been measured as a function of temperature. The displacement of SH mode is perpendicular to the propagation direction. The FLCs used in the experiment have several phases in the measured temperature range from room temperature to isotropic phase. The phase delay difference decreases with the cell temperature, in the case of the rubbing direction perpendicular to the propagation direction. This result indicates that the viscosity component parallel to the alignment direction of the cell is essentially related with the velocity change. Two viscosity components, parallel and perpendicular to the alignment direction, have been discussed in some liquid crystalline phases.

D1P.14

SOFT MODE DIELECTRIC RELAXATION UNDER THE INFLUENCE OF BIAS ELECTRIC FIELD OF A FERROELECTRIC LIQUID CRYSTAL MIXTURE, S.Sinha Roy, T. Pal Majumder, and S.K.Roy, Department of Spectroscopy, I.A.C.S., Jadavpur, Calcutta-700 032, India.

Temperature dependence soft mode part of the complex dielectric constant has been measured as function of bias electric field and cell thickness in the smectic-A\* phase. From the experimental data soft mode relaxation frequency and dielectric strength have been determined both in smectic C\* and smectic A\* phases. Dielectric result shows a weak dependence of soft mode dielectric strength and relaxation frequency with bias field, except near to the transition temperature. It is found that near to the transition temperature in the Sm-A\* phase, relaxation frequency increases with increasing bias field while the corresponding dielectric strength decreases. It is also observed that surface effect does have a little influence on the dielectric strength of the soft mode in Sm-A\* phase.

D1P.15

DIELECTRIC, SPONTANEOUS POLARIZATION AND TILT MEASUREMENTS IN FERROELECTRIC LIQUID CRYSTALS

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We report spontaneous polarization, tilt, rotational viscosity, switching time and broadband dielectric measurements on the 2'-[6'-((2"S-2"-chloro-3"-methylbutanoyl)oxy)]-naphthyl-4-decyloxybenzoate ferroelectric liquid crystal. Six different relaxations have been obtained and characterized: soft mode, Goldstone mode, ferroelectric domain mode, reorientation of molecular long axis around short axis, rotation around molecular long axis and a high frequency relaxation that could be related to librational motions. We used the dielectric results together with polarization an tilt measurements to obtain some of the parameters of the free energy expansion corresponding to the Landau generalized model.

[1] T. Sierra, J.L. Serrano, B. Ros, A. Ezcurra, J. Zubia, J. Am. Chem. Soc. 114, 7645 (1992).



DYNAMICAL PROPERTIES OF TWO FERROELECTRIC PHASES OF EPOXY COMPOUND, M.Marzec\*, A.M.Biradar\*, R.Dabrowski<sup>5</sup>, B.Gestblom®, M.Godlewska\*, W.Haase\*, S.Hiller\* and S.Wróbel\*, "Jagellonian University, 30-059 Kraków, Poland; "National Physical Laboratory, New Dehli-11012, India; "University of Uppsala, Sweden; WAT, Warsaw, Poland; "TH Darmstadt, Germany.

Dielectric methods (FDDS and TDS) were used to study collective and molecular processes of two ferroelectric phases of 4'-[(S,S)-2,3-epoxyhexyloxy] phenyl 4-decyloxy benzoate (EHPDB) which shows the following phase sequence: Is-N\*-SmC\*-S<sub>3</sub>-Cr. In our previous study [1] of this material it has been shown that the S<sub>3</sub> phase is also a ferroelectric one. In this study new dielectric measurements have been done using gold coated cells which allowed to observe the soft mode in the N\*-SmC\* pretransition region. The Goldstone mode was observed for the SmC\* and S<sub>3</sub> phases, however, the S<sub>3</sub> phase appears to be a metastable one. TDS spectroscopy allows to detect the dielectric spectrum connected with molecular reorientation. Critical frequencies and dielectric increments are presented for all processes observed and discussed in terms of the mean-field model. Metastability of the S<sub>3</sub> phase detected by FDDS, DSC and polarizing microscopy is discussed in terms of Avrami model.

[1] M.Marzec et al., Ferroelectrics, in print Supported by KBN grants: 2 P302 139 07 and 2 P03B 101 09 and Polish Germany Project BMBF (st 080.1)

# D1P.17

CONFORMATION ANALYSIS OF FERROELECTRIC LIQUID CRYSTALS BY USE OF <sup>2</sup>H-NMR

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Synthesis and  $^2$ H-NMR conformational analysis of a ferroelectric liquid crystalline molecule with selectively deuterated chiral alkyl chain ( $\alpha$ -methyl alkyloxy chain) will be reported. The spectrum in SmA and SmC phases consists of a superposition of well resolved quadrupolar doublets, while that in a low-temperature SmX phase consists of a two-fold flip-flop pattern. The observed quadrupolar splitting profile is analyzed based on the molecular orbital calculation data. The MO calculation predicts the formation of two possible conformations (linear and bent), while the  $^2$ H-NMR analysis indicates that the linear chain conformation is selected in smectic phases. The formation of linear chain conformation in fluid smectic phases (A and C) is generally expected for all FLC molecules with the  $\alpha$ -methyl alkyloxy chain. (\*corresponding author)

# D1P.18

FT-IR STUDIES OF THE SWITCHING DYNAMICS OF FLC DEVICES.

G. K. Bryant, H. F. Gleeson, A. Yasuda\* & D. Reimer\*

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\*Sony Corporation Research Centre, Yokohama, Japan

The switching dynamics in ferroelectric liquid crystal devices have been monitored on a microsecond time scale using time-resolved FT-IR spectroscopy. Molecular reorientation was investigated with respect to temperature and with differing applied switching voltages. Measurements were taken for three related FLC's, all simple three-component systems consisting of chiral molecules of 5wt% and two kinds of phenyl pyrimidine each of 47.5wt%. The polariser was set at 45° to the aligning direction and spectra were collected with a time resolution of 1µs. Two vibrational modes are considered corresponding to the core and alkyl chain of the molecule respectively. Data are normalised with respect to the 'field off' intensity in order to estimate the relative movement of these two parts of the molecule during the switching process. Results indicate that in general the molecule reorients as a unit, although some interesting effects are seen in the response of the core to increasing field strength.

A COMPARATIVE STRUCTURAL STUDY OF THREE PERSPECTIVE LONGITUDINAL FERROELECTRIC SMECTIC LIQUID CRYSTALS<sup>†</sup>, Yushan Shi, Joseph Mang, & Satyendra Kumar, Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

A longitudinal ferroelectric smectic phase possesses spontaneous polarization parallel to the director, which may be achieved with appropriate chemical design of molecules. Using x-ray diffraction, we have examined three systems: a fraternal-twin triester synthesized at Kent[1], a mixture of polyphilic compounds[2], and cyclic siloxane co-oligomer[3]. These systems exhibit properties of longitudinal ferroelectric phases to varying degrees. A comparative structural analysis of these materials will be presented, which should be of value in future design and development of such novel materials.

<sup>†</sup>Work supported by NSF ALCOM grant DMR-89-20147.

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- [2] F. Tournilhac, L.M. Blinov, J. Simon, & S.V. Yablonsky, Nature, 359, 6396 (1992).
- [3] H. Wang, M.Y. Jin, R.C. Jarnagin, E.T. Samulski, T.J. Bunning, W. Adams, B. Cull, Y. Shi, S. Kumar, preprints.

D1P.20

NON-ORTHOGONAL PHASES IN FERROELECTRIC AND ANTIFERROELECTRIC LIQUID CRYSTALS V.L. Lorman, Laboratoire de Physique de la Matière Condensée, Université de Picardie, Amiens, France

The structure analysis and physical properties of the ferroelectric smectic phase with an angle between the polarization and the projection of a big molecular axis (c-director) different from 90° are presented. It is shown that classical SmC\* phase can transform itself into the non-orthogonal one through the second order phase transition. Corresponding additional soft mode is associated with scalar product  $V = (\eta P)$  of the c-director  $\eta$  and the polarization P. The value of V varies with temperature in the non-orthogonal phase leading to the different temperature dependencies of the apparent tilt angle and of the polarization. Analogously, there exists an additional (non-orthogonal) antiferroelectric phase with two smectic layers in the unit cell. It is characterized by the temperature dependent angle between  $\eta_A = \eta_1 - \eta_2$  and  $A = P_1 - P_2$ , where  $\eta_i$  are the c-directors and  $P_i$  are the polarizations in the consecutive layers. Thus, in the framework of the two-layer model [1] there exist two different antiferroelectric phases. Their dielectric and optical properties can be compared to those of SmC<sub>A</sub>\* and Sm(AF) phases in the series of mixtures of the MHPOBC-type (f.e. MHPOCBC with MHPOCCBC)[2].

- [1] H. Orihara and Y. Ishibashi, Jpn. J. Appl. Phys. 29, L115 (1990)
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D1P.21

PHASON DYNAMICS OF FERROELECTRIC LIQUID CRYSTALS UNDER DC ELECTRIC FIELD, Y. Kimura, H. Inoue and R. Hayakawa, Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, JAPAN.

We have studied the dynamics of the phason (Goldstone) mode in the Smectic C\* phase of ferroelectric liquid crystals by the dynamic light scattering spectroscopy. The correlation frequency obtained from the auto-correlation function of the scattered light intensity without an applied dc electric field shows a parabolic dispersion as a function of scattering wavenumber, which is in good agreement with that calculated from the phenomenological equation of motion. From this comparison are obtained the temperature dependences of the ratio of elasticity to viscosity and the helical pitch. Under a dc electric field, there appears a frequency gap at the half of the wavenumber of the helical structure and the gap frequency increases in proportion to the dc field. The monotonic dispersion is observed above the critical dc field where the helix is completely unwound. The existence of a gap in the phason dispersion due to the break of translational symmetry under external field has been theoretically predicted [1] and confirmed by comparison between the magnetic field dependence of the dielectric relaxation time and the correlation time obtained from the light scattering under the magnetic field [2]. Our experimental results are in good agreement with the theoretical ones.

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200nsec TIME-RESOLVED FT-IR STUDY OF FERROELECTRIC LIQUID CRYSTALS

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This paper reports the development of 200nsec FT-IR time-resolved spectroscopy (FT-IR TRS) and its application to the study of liquid crystal reorientation dynamics. The system consists of a Bio-Rad FTS6000 FT-IR spectrometer equipped with a DC-MCT detector, a high-speed pre-amplifier and a 10MHz A/D converter. The application of this 200nsec FT-IR TRS system to the study of transition dynamics of ferroelectric liquid crystals has revealed that the flexible alkyl chain appended to a core moiety undergoes a fast local motion in addition to the overall reorientational motion of the molecule as a whole. It should be emphasized that this result demonstrating the presence of internal conformational transition during the field-induced reorientation of liquid crystals is obtained by taking the advantage of fast FT-IR TRS technique that can provide both temporal and spectral information.

# D1P.23

PRINCIPLES OF FERROELECTRIC LIQUID CRYSTALS ELECTROOPTICAL RESPONSE TIME MINIMIZATION, <u>E.P.Pozhidaev</u>, A.L.Andreev, A.I.Pavluchenko\*, I.N.Kompanets, L.A.Kutulya,\*\* P.N.Lebedev Physical Institute, Leninsky pr.53, Moscow, 117924, Russia; \*Organic Intermediates & Dyes Institute, B.Sadovaya, 1-4, Moscow, 103787, Russia; \*Institute for Single Crystals, Leninsky pr.60, Kharkov, 310001, Ukraine.

Principles of FLC's electrooptical response time minimization on the base of multicomponent mixtures optimization are discussed. They are: 1) selection of optimal chemical compounds, both chiral and nonchiral; 2) search of optimal concentration of each compound in the mixture[1]. The way of  $\gamma_{\varphi}/P_s(T)$  dependence weakening due to the special choice of mixture components is proposed also( $\gamma_{\varphi}$ -rotational viscosity,  $P_s$ -spontaneous polarization, T-temperature). FLC light shutters with electrooptical response time 2,5 mks and contrast ratio more than 200:1 in a white light (T=25°C, driving voltage  $\pm 40$ V) were made by a result of our attempts.

A.L.Andreev, N.I.Chernova, I.N.Kompanets, M.V.Loseva, A.V.Parfenov, A.I.Pavluchenko, E.P.Pozhidaev, SPIE, 2051, 212 (1993).

# D1P.24

VOLUME BISTABILITY IN FERROELECTRIC LIQUID CRYSTAL DROPLETS, V.Ya.Zyryanov, S.L.Smorgon, V.F.Shabanov, A.L.Andreev\*, E.P.Pozhidaev\*, I.N.Kompanets\*, L.V.Kirensky Institute of Physics, Krasnoyarsk, 660036, Russia; \*P.N.Lebedev Physical Institute, Leninsky Pr. 53, Moscow 117924.

The effect of volume bistability (VB) has recently been discovered and analysed [1] in thick (15 mcm and more) layers of purposefully created ferroelectric liquid crystal (FLC) compositions. VB is a phenomenon that is mainly associated with the stereochemical nature of the FLC composition and is practically independent of the surface. We have studied the characteristics of planar-oriented PDFLC films obtained based on the above compositions. The effect of VB is shown to take place in large-size droplets. Unlike pure layers, VB in FLC droplets is of a reverse nature, i.e. an optical state is memorised that is opposite to the optical state corresponding to the polarity of the driving pulse. We discuss the features typical of VB in FLC droplets and make a comparison between the results obtained and the results of surface bistability studies in FLC droplets [2].

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BISTABLE SWITCHING AND THE TEMPERATURE DEPENDENCE OF THE ANCHORING ENERGY, Stefan Markscheffel and Alfred Saupe, Max Planck Research Group, Liquid Crystalline Systems at Martin Luther University, Mühlpforte 1, Halle/S 06108, Germany

We prepared ferroelectric liquid crystal cells in bookshelf orientation of the smectic layers between silane treated surfaces [1]. The switching behavior of a short pitch (0.43 $\mu$ m) chiral smectic C liquid crystal mixture was studied as a function of the applied pulse width  $\tau$  and the temperature T [2]. Bistable switching was observed in the  $S_C^*$ -phase over a broad temperature range. The threshold voltage for bistable switching  $U_{th}$  was strongly dependent on the applied pulse width and the temperature. Using the relation  $U_{th}(\tau)=U_{DC}+const/\tau$  and previous data on the elastic constant [3] we estimated the anchoring energy thres-hold  $W_0$ . It varies within the experimental error linearly with the temperature and probably changes it's sign at around 50  $^{O}$ C. The sign reversal of  $W_0$ , connected with a change of the plane of bistability, will be discussed.

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D1P.26

TILTED SMECTIC LAYERS ON HOMEOTROPICALLY TREATED PLATES OF A SMC\* LIQUID CRYSTAL, M. Giacondo, A. Jákli\*\* and A. Saupe\*, Unical Liquid Crystal Group, Dipartimento di Fisica, Universita della Calabria, 87036 Arcavacata di Rende - Cosenza, Italy, \*\*present address: Research Institute for Solid State Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P. O. Box 49, Hungary, \*Max Planck Research Group, Liquid Crystal Systems, Mühlpforte 1, 06108 Halle/S, Germany

We observed formation of uniformly tilted smectic layer structure in SmC\* films on homeotropically treated plates. The layer tilt increases from zero to 14° as the sample is cooled from the smectic A to room temperature. Such structures show polar electro-optical switching confirming that the permanent polarization has a component parallel to the applied field.

Our calculations indicate that the layer tilt is mainly due to the balance between the surface tension (that prefers horizontal layers) and the homeotropic surfactant (that promotes the director to be normal to the plates).

\*the experiments were carried out in the Max Planck Research Group, Liquid Crystal Systems, Halle, Germany in the frame of Europen Network for Macroscopic Properties of Liquid Crystals.

D1P.27

SWITCHING BEHAVIOUR AND ELECTROOPTIC RESPONSE OF A FERROELECTRIC LIQUID CRYSTAL MIXTURE, A.Mukherjee and S.L.Srivastava, Physics Department, Allahabad University, Allahabad - 211002, INDIA.

Switching time ts, spontaneous polarization Ps, torsional bulk viscosity  $\gamma t$ , tilt angle  $\theta$  in SmC\* phase and induced tilt angle  $\theta$  ind in SmA\* phase for a low pitch 10 $\mu$ m thick planar oriented mixture FLC#252 measured in the temperature range 25-58°C are Ps=34.22(Tc-T) nC/cm,  $\theta$ =16.61(Tc-T) and E/ $\theta$ ind=4.9469x10(T-Tc)Vm<sup>-1</sup> degree<sup>-1</sup> where Tc=51.4°C. The critical field for unwinding the SmC\* phase helix is 1.89±0.07 kV/cm for 25<T<44°C and on further heating becomes almost zero at about 51°C. ts lies in the range of 36-2 msec for electric field between 1 to 7 kV/cm. The ratio of mobility of the charge carriers to the domain size is  $\phi$ /D=0.7451x10<sup>-2</sup>(Tc-T) mV<sup>-1</sup> sec<sup>-1</sup>.  $\gamma$ t is nearly 100 times larger than the rotational viscosity  $\gamma \phi$ .

INFLUENCE OF THE SURFACE ANCHORING ENERGY ON THE SMECTIC LAYER FORMATION IN FERROELECTRIC LC, <u>V. P. Vorflusev\*</u> and H.-S. Kitzerow, Iwan-N.-Stranski-Institute, TU, Sekr. ER 11, Str. des 17. Juni 135, 10623 Berlin, Germany.

We have investigated the influence of surface treatment on the memory angle  $\Theta_m$  [1] in chevron FLC-cells. Surface anisotropy was produced either by UV illumination or by rubbing of a PVA layer containing an azo dye. Different azimuthal anchoring energies of the FLC on the substrate can be obtained by different exposure times and different pressure during the rubbing process, respectively. Due to the low pretilt angle ( $\Theta_p < 2^{\circ}$ ), we suppose that the measured value of  $\Theta_m$  is governed by the tilt angle  $\delta$  of the smectic layers. A model is presented which relates the equilibrium value of  $\delta$  to a balance between the azimuthal anchoring energy and the bend energy of the smectic layers in the chevron structure.

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#### D1P.29

VERY LOW POWER AND HIGH SPEED LIQUID CRYSTAL FABRY PEROT ETALONS USING DEFORMED HELIX FERROELECTRIC LIQUID CRYSTALS. <u>W.K. Choi</u>, A.B. Davey and W.A. Crossland. Cambridge University Engineering Department, Trumpington street, Cambridge CB2 1PZ, England.

We have recently demonstrated [1] that Deformed Helix Ferroelectric Liquid Crystals (DHFLCs) [2] can be used in Fabry Perot etalons to produce high speed optical switches and wavelength tunable filters. The DHFLC used was Roche FLC6304 with pitch length of 0.35µm. In this paper, we show that both the response times and the wavelength tuning range reported have been improved significantly by using a shorter pitch DHFLC (Roche FLC 9848, 0.15µm). They offer the fastest switching speeds (<100µs) and also require the lowest operating voltages (<2V/µm) among all other Sm\*C Ferroelectric Liquid Crystal Fabry Perot etalons that have been reported so far [3,4]. Thus they are highly attractive to be used in high speed applications, such as liquid crystal on silicon VLSI, where the supply voltages are limited. In addition, comparisons and discussions between the results obtained using the two different pitch length DHFLCs and different thicknesses of cavity will also be made.

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# D1P.30

AN OBSERVATION OF THE EFFECT OF THE SURFACE TOPOGRAPHY ON THE DEFECT DENSITY IN SMC\* DEVICES J.Pirs, S.Kralj, S.Pirs, B.Marin Jozef Stefan Institute, Ljubljana, Slovenia and P.Watson, C.Hoke, P.Bos Liquid Crystal Institute, Kent, Ohio, USA

The effects of the surface topography on the defect density in surface stabilized SmC\* thin film liquid crystalline layers was studied. It was found that even very small orienting surface defects can cause the instability of the chevron structure as long as the slope of these defects is high enough. The studies were performed on the standard 1.5 um thick SSFLC display cells using rubbed nylon as the orienting layer and Hoechst Felix-013 ferroelectric liquid crystals. Various origins of the orienting surface topography "defects" have been studied from different nylon application methods to various temperature cycling causing excessive polymer crystallization. Different techniques have been developed to cure this phenomenon including polymer modification as well as heat quenching. The orienting surfaces as well as the polymer crystallization originating surface irregularities were studied by AFM as well as SEM microscopy methods. The results show excellent correlation between the surface topography and chevron structure defects density in the ferroelectric liquid crystal oriented by such surfaces. A simple theoretical model for the influence of the surface topography on the chevron structure in the SmC\* liquid crystals, showing strong hysteresis phenomena, was developed and its predictions compared to the experimental results. (work supported in part by grant NSF DMR 8920147)

CHEVRON PRETRANSITIONAL PHENOMENA, A. N. Shalaginov, Department of Physics, Marine Technical University, Leninsky pr. 101, St. Petersburg 198262, Russia.

There have been a number of recent studies of liquid crystals confined between parallel boundary plates in the so-called chevron structures. The chevron structure develops when the mismatch  $\epsilon$  exceeds some critical value  $\epsilon_{cr}$  [1], where  $\epsilon = 1 - q/q_0$ , q and  $q_0$  are the reciprocal layer spacings at the interfaces and in the bulk. The dynamical model of the formation the chevron structure starting from the bookshelf structure in the smectic-A liquid crystal has been proposed elsewhere [2].

In this work I study pretransitional phenomena in the bookshelf structure for  $\epsilon$  close to its critical value. I calculate the correlation function of the smectic layers undulations. The correlations show the critical behaviour typical for second order phase transitions. This undulations manifest themselves in diffuse x-ray scattering (see, for example, [3]) and in light scattering experiments. I discuss possible x-ray and light-scattering experiments where the theory can be applied.

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D1P.32

FIELD INDUCED PUMPING GENERATES PRESSURE CHANGES IN A FERROELECTRIC LIQUID CRYSTAL CELL, Z. Zou and N.A. Clark, University of Colorado, Physics Department and OCS Center, Boulder, CO 80309, USA.

Molecular rotation generates mass flow in liquid crystals [1]. For certain cell geometries and applied voltages, a net flow or pumping effect can be observed in ferroelectric liquid crystals [2]. The pumping effect is induced by the molecular rotation which couples with the changes of the hydrostatic pressure. Recently, Jakli et al reported [3] cell thickness changes under the applied AC electric field to a FLC cell, indicating a flow induced stress normal to the bounding plates. In this work, we study the pressure behavior in a SSFLC cell under applied electric fields. The Leslie equations [1] are solved numerically to calculate the pressure and stress.

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- \* This work is partially supported by CATI 960002 and NSF MRG grant DMR 9224168.

D1P.33

X-RAY ANALYSIS OF PHOTOMECHANICAL EFFECTS IN FERROELECTRIC LIQUID CRYSTALS: UV-INDUCED STRUCTURAL CHANGES IN AZOBENZENE-DOPED CE8, <u>E A Corsellis</u> & D Guillon, Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, F-67037 Strasbourg Cedex, France

Light-induced structural changes in a lamellar liquid crystal matrix doped with photochromic moieties have been reported to result in controllable variations of mesophase properties (such as spontaneous polarisation) and reversible, isothermic phase transitions [1]. These mechanisms have been proposed as the basis for optically-controlled optical switches and holographic memory devices. Photomechanical effects in a ferroelectric liquid crystal matrix, CE8, containing an azobenzoic liquid crystalline dye, N5, have previously been investigated via the bulk optical and electrical properties of the system [2]. The current work presents a study of these effects at the microscopic level using simultaneous illumination by an x-ray beam and a near-ultraviolet photoisomerising source. The development of the light-induced structural changes during illumination and the subsequent relaxation are discussed.

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SMECTIC LAYER ROTATION BY ELECTRIC FIELD IN FERRO- AND ANTIFERROELECTRIC LIQUID CRYSTALS, Keizo Nakayama, Masanori Ozaki and Katsumi Yoshino, Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka 565, Japan

We have investigated a reversible rotation of smectic layer in the ferroelectric and antiferroelectric chiral smectic C phase as a function of an applied voltage waveform, cell geometry and molecular structure. The layer rotation is caused by applying asymmetric pulses of electric field and the direction of the rotation depends on the waveform of the applied field. The smectic layer rotates regardless of the surface condition of substrates, while the rate of rotation depends on material. A monodomain alignment can be maintained within the rotation angle of about 20° and over that angle, turns into a multidomain, while some domains can rotate over 90°. The rotation direction of R-configuration is opposite to that of S-configuration of the same liquid crystal under applying the same form pulses. Namely, the rotation direction depends on the sign of spontaneous polarization. In addition, we have observed the layer rotation by applying DC voltage, which might be caused by a flow of impurity.

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# D1P.35

THE REASON AND CONDITIONS OF THE VOLUME BISTABILITY EFFECT IN FERROELECTRIC SMECTIC C\* LIQUID CRYSTALS, <u>E.P.Pozhidaev</u>, A.L.Andreev, I.N.Kompanets, P.N.Lebedev Physical Institute, Leninsky pr. 53, Moscow, 117924, Russia.

The volume bistability (VB) effect has been observed by us earlier[1]. The comparative analysis of the volume bistability and the surface one has been reported[2]. Now we discuss stereochemical conditions of the effect existance and principles of composing VB FLC multicomponent mixtures. A thermodynamical description of the effect is proposed, a potential barrier between two stable states of the VB FLC is evaluated. It was shown, that the barrier value depends stronghly on VB FLC chemical structure, but quite independent on boundaring surfases nature, boundary conditions and on the FLC layer alighnment quality, when the FLC layer thickness is more than 50 mkm. The combined volume-surfase bistability (VSB) is considered when the potential barrier is formed due to both boundaring surfaces and the FLC volume.

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# D1P.36

SPONTANEOUS TRANSITION FROM CHEVRON TO UNIFORMLY TILTED LAYERS IN FERROELECTRIC LIQUID CRYSTALS, <u>I.C. Jones</u>, K.P. Lymer, L. Taylor\*, P.E. Dunn, S.D. Haslam and R.M. Richardson\*, Defence Research Agency (DRA), St. Andrews Rd., Malvern, Worcs. WR14 3PS, UK.

Most ferroelectric liquid crystal devices use the chevron geometry [1], in which the smectic layer normal is tilted with respect to the substrates in opposite directions in either half of the cell. This structure is believed to be due to the combined effect of shrinkage of the smectic layer spacing on cooling through the smectic C or smectic C\* phases, and surface pinning of the layers at some temperature in the overlying smectic A phase. Asymmetric chevrons may result from anti-parallel aligned cells with a large surface pretilt [2], or by externally disturbing the symmetric chevron [3]. In this work, a spontaneous transition from a chevron state to a uniform tilted layer is observed using optical and X-ray techniques. The occurrence of this transition is may be prevented with very small changes to the material structure. It is proposed that the transition occurs for materials where the energy associated with the smectic layer distortion at the chevron interface exceeds the layer surface energy.

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# STUDIES ON SWITCHING DYNAMICS IN THE VICINITY OF SMECTIC C\* - SMECTIC I\* CRITICAL POINT, Geetha G.Nair and S.Krishna Prasad, Centre for Liquid Crystal Research, Jalahalli, Bungalore 560 013

We report ferroelectric switching time measurements near the smectic C\*-smectic I\* critical point observed by us recently[1]. The technique employed enables separation of the contribution from exexisting phases at the transition. This allows one to follow the jump in the switching time at the transition as a function of concentration on approaching the critical point. Results show that the two " paths of approach " to the critical point via., the jump in switching time versus the effective transition temperature and the thermal variation of the switching time at the critical concentration, can be described by powerlaw expressions. The exponents obtained are compared with theoretical predictions and also with the results of dynamic specific heat experiments[2] near such a critical point.

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D1P.38

COMPUTER SIMULATIONS OF SURFACE STABILISED FERROELECTRIC LIQUID CRYSTALS, D.R. Binger and S. Hanna, Physics Dept, Bristol University, Tyndall Avenue, Bristol, BS8 1TL, UK.

Computer Simulations have been carried out to investigate the behaviour of monolayers of surface stabilised ferroelectric liquid crystals (SSFLCs) on polymer substrates. SSFLCs are interesting because of their use in a new generation of high speed displays. For these, an optical cone angle close to 45° is desirable, but the actual cone angle obtained depends on the polymer substrate used. Much experimental work has already been carried out to identify which polymers perform best [1]. The aim of our work is to understand the interactions between the polymer and the liquid crystal molecule, at a molecular level, in order to be able to predict which polymers will give useful cone angles. The systems we have examined consist of nylon and polyethylene (PE) substrates, using the ferroelectric liquid crystal MBF which forms a SmC\* phase when suitably doped. Molecular dynamics simulations have been performed using the microcanonical ensemble and run for a range of different times up to 2ns. PE was examined most extensively, with simulations including both isolated liquid crystal molecules and small clusters. Although the systems were too small to observe any large scale behaviour, such as phase transitions, some alignment was observed between the liquid crystal molecules and the substrate within the simulation times used, allowing an estimate of the cone angle to be made. By examining different polymer substrates, it will be possible to establish which aspects of the surface structure lead to a useful cone angle.

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D1P.39

MODELLING OF SURFACE-STABILIZED FERRIELECTRIC LIQUID CRYSTAL CELLS, J.M. Otón, and <u>Jorge Sabater</u>, Departamento de Tecnología Fotónica, ETSI Telecomunicación, Ciudad Universitaria, E-28040 Madrid Spain

In this work, two models of ferrielectric liquid crystals are presented. If no voltage or a constant voltage is applied to the cell, a static model can be used. The system is then described by the layer angle distribution, the internal voltage and the azimuthal angle of each layer. Six smectic layers are considered for describing the system. In these circumstances, the ferroelectric and antiferroelectric phases [1] are just particular cases of the ferrielectric model. Phase stability as a function of the interlayer coupling constant, spontaneous polarization, and applied voltage is studied. The second, dynamic, model employs a simplified description with only three layers, but includes viscosity terms, thus allowing the study of switching characteristics and hysteresis curves of ferrielectric devices.

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SWITCHING OF SURFACE-STABILIZED FERROELECTRIC LIQUID CRYSTAL CELLS BY MOTION OF DEFECTS, Thorsten Seitz, Joachim Stelzer, and <u>Hans-Rainer Trebin</u>, Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57/VI, D-70550 Stuttgart, Germany

Very exact numerical calculations are presented on switching processes of surface-stabilized ferroelectric liquid crystal cells. In particular defect mediated switching by Bloch walls and by disclination lines is studied. Our examinations are based on an idealized bookshelf-configuration of the molecules with fixed tilt angle of the director. Solutions for the scalar fields both of the director twist angle and the electric potential have been determined in two spatial dimensions, assuming the fields to be constant along the third dimension. In the bulk we employ the full Frank-Oseen energy (i.e. no one-constant approximation) with electric terms added represented by an uniaxial dielectric tensor and the spontaneous polarization. On the surface the director is anchored by a Rapini-Papoular potential with medium anchoring strength. The calculations were performed in high precision with a multigrid method on an adaptive grid.

# D1P.41

THE STUDY OF ALIGNMENT CHARACTERISTICS OF THE TWIST FERROELECTRIC LIQUID CRYSTALL, <u>Jianxin Guo</u>, Weishong Zhao, Sheng Wu, Zhenjun Ma, Ximin Hang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021

By exciting strong reflection optical guided mode, the alignment characteristics of ferroelectric liquid crystal aligned by evaporated SiOx layers in cells with different thickness were studied. The high reflection metal layer was used as substrate in the experiment and the reflection signals were enhanced by it. The 4×4 transfer matrix method presented by Berreman<sup>[1]</sup> is used to analysis liquid crystal layer treated as a multi-layered uniaxial medium. The detailed director configuration of twist structure was well detected and the reasons were discussed.

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# D1P.42

KINK SWITCHING IN SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTALS, <u>E.S. PIKINA#</u>, E.L. DEMIKHOV+ and S.A. PIKIN\*, \*Inst. of Crystallography, Russian Acad. of Sciences, 117333 Moscow, Russia; + Inst. of Phys. Chem., Univ. of Paderborn, 33095 Paderborn, Germany; # Inst. of Oil and Gas, Leninski pr. 63, 117917 Moscow, Russia

Dynamics of director field switching in the vicinity of the SmA-SmC\* phase transition is studied by means of a light scattering technique [1]. The resonance dependence of scattered intensity on the electric field frequency is observed. The dynamics of ferroelectric liquid crystals in an electric field is determined by the inherent collective exitations which exist in the system equilibrium (Goldstone and Soft modes) or can be produced in a field. Because the switching angle in the surface stabilized geometry is large and conditions for the director motions on the anchoring substrate and in the bulk are not equivalent, the switching process may involve the production of inhomogeneities in the director orientation which propagate from one sample boundary to the other. One of the simplest forms of such inhomogeneities is so-called kink of the director field orientation across the film. If the kink propagation time coincides with the period of the a.c. electric field, light scattering of the resonance type can be expected. The observed resonant light scattering in the low frequency region can not be explained as scattering by the Goldstone mode. The kink switching model describes successfully the resonance profile and its dependence on temperature and electric field.

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X-RAY DIFFRACTION STUDIES OF SURFACE-STABILISED FERROELECTRIC LIQUID CRYSTAL DEVICES (SSFLCDS), J.Ebbutt, L.Taylor and R.M.Richardson, School of Chemistry, University of Bristol, Bristol, U.K., S.D.Haslam and J.C.Jones, Defence Research Agency, St. Andrew's Road, Great Malvern, Worcestershire, WR14 3PS, U.K.

X-ray rocking curve experiments have been performed as a function of temperature to enable us to understand how the layer structure of the  $S_c$  phase forms from the bookshelf  $S_A$  geometry in SSFLCDs. Studies [1 and refs. therein] suggest that layer thinning caused by director tilt away from the layer normal occurs below the A-C transition. To investigate the influences of surfaces we study low and high pretilt cells with parallel and anti-parallel arrangements, using the FLC materials SCE13 and SCE8. In the  $S_A$  phase in high pretilt cells, a conflict exists between the formation of the bookshelf structure and some other tilted geometry. In SCE13, the tilted structure dominates in high pretilt parallel cells, whereas a uniform tilted layer (UTL) structure is observed in anti-parallel cells. In the  $S_C$  phase, all parallel and low tilt anti-parallel cells give the expected chevron structure. High tilt anti-parallel cells give an unusual tilted chevron arrangement in conjunction with a UTL.

1. Y.Yamada, Y.Yamamotu, T.Inoue, H.Orihara and Y.Ishibashi, Jpn. J. Appl. Phys., 28, 50, (1989)

D1P.44

SURFACE ANCHORING INFLUENCE ON POLARIZATION SWITCHING PROPERTIES OF SSFLCS, A. Mochizuki, T. Makino, H. Shiroto, Y. Kiyota and T. Yoshihara, Display Lab., FUJITSU LABS. LTD. 64 Nishiwaki, Ohkubo, Akashi 674 Japan

Polarization switching properties of SSFLCs in terms of the surface anchoring effect were investigated. The effect on the polarization switching was clarified by setting the following parameters; pre-tilt angle at the interface between alignment layer and the liquid crystal molecule: layer structure in SmC\* phase of the FLCs: compression and expansion environments to the FLC cells. Low frequency and low voltage trianguler waveform applications on to each pre-tilt cell suggests that the low pre-tilt chevron geometry provides stronger surface anchoring effect. Low pre-tilt bookshelf geometry which is realized by the naphthalene-base FLCs[1] indicates whole LC molecule's switchings including the interface area. This conclusion is also supported by the polarization switching study under the compression and expansion environments.

[1] A. Mochizuki et. al.; Ferroelectrics, 113, 353 (1991); 122, 37 (1991), Mol. Cryst. Liq. Cryst. 243, 77 (1994).

D1P.45

USE OF PTFE ALIGNMENT LAYERS IN PASSIVE ADDRESSED SSFLC DISPLAYS, F. Campoli, R. Beccherelli, A. d'Alessandro, V. Ferrara, A. Galloppa, A. Galbato, P. Maltese, Department of Electronic Engineering, La Sapienza University and National Institute of Physics of Matter, Rome, 00184 ITALY.

Polytetrafloroethylene (PTFE or Teflon) layers have been developed as orientation films in order to produce ferroelectric liquid crystals displays with improved addressing behaviour. Teflon layers have been friction deposited on glass substrates with ITO electrodes at various temperatures in the range 150-180 °C. The PTFE layers have been used to assemble displays which were addressed and showed no hysteresis, reduced image sticking and reduced switching time with respect to standard test cells employing rubbed polymers as alignment layers. In order to assure the best electro-optical performance, PTFE films have been characterized from the point of view of uniformity and thickness as a function of deposition parameters. At present we use teflon layers in analog grey scale devices, in which one of the glass substrates employed to assemble the cell has a high resistivity inorganic oxide layer which produces a transversal electric field gradient across the pixel.



MATRIX ADDRESSING WAVEFORMS FOR GREY SHADES SSFLC DISPLAYS <u>V. Ferrara</u>, R. Beccherelli, F. Campoli, A. d'Alessandro, A. Galloppa, A. Galbato, P. Maltese, Department of Electronic Engineering, La Sapienza University and National Institute of Physics of Matter, Rome, 00184 ITALY.

To produce analog grey shades in our special construction SSFLC matrix display, different "low voltage", "stopped writing" and "hampered writing" addressing waveforms have been tested in computer simulations and experiments. Three phenomena limit the achievable results, one is addressing hysteresis, subject of our previuos paper, the second is crosstalk from data intended for other pixels, the third is characteristic switching pulse area variations due to cell temperature or thickness variations. We present here computer simulations of the two latter effects, for a range of different addressing modes and data modulation techniques. For the faster addressing modes, based on liquid crystal dielectric biaxiality, data waveforms are necessary featuring constant rms voltage, dc balance and crosstalk compensation. A new technique will be introduced making use of such data waveforms in place of the previous ones, based on amplitude or pulse-position modulation.

# D1P.47

ADVANCES IN FERROELECTRIC LIQUID CRYSTAL MATERIALS AND THEIR APPLICATION IN DEVICES, Michael D. Wand, William N. Thurmes, Kundalika M. More, and Rohini T. Vohra, Displaytech Inc., 2200 Central Ave., Boulder, CO 80301

Ferroelectric smectic C\* liquid crystals have been shown to exhibit a high speed electrooptic response when used in the surface stabilized ferroelectric liquid crystal (SSFLC) geometry. SSFLC devices afford an array of applications ranging from simple single-element light shutters used in stop-action photography, stacked single element shutters useful in switchable color filters capable of turning monochrome CRTs into full color displays, and multiple element high resolution microdisplays fabricated on the surface of a Dynamic Random Access Memory chip. Several new classes of FLC materials will be reported and their performance discussed with respect to their use in various optoelectronic applications.

#### D1P.49

PERFORMANCE PARAMETERS OF PIXELLATED ANALOGUE OPTICALLY ADDRESSED SPATIAL LIGHT MODULATORS, <u>L.W.K. Yim</u>, A.B. Davey and A.R.L. Travis, University of Cambridge, Engineering Department, Trumpington St, Cambridge, CB2 1PZ, UK.

We have fabricated pixellated analogue Optically Addressed Spatial Light Modulators (OASLMs) using the twisted smectic C\* liquid crystal effect which has been described to show intrinsic grey-scale response in both transmission and reflection modes [1]. In our OASLM, the photosensor is intrinsic amorphous silicon (a-Si:H) which forms a Schottky barrier with the Indium Tin Oxide (ITO) transparent electrode. A layer of aluminium pixellated metal mirrors is used between the photosensor and the twisted smectic C\* liquid crystal layer to enhance the reflectivity of the device. The twisted ferroelectric liquid crystal effect relies on a high liquid crystal cone angle of about 45°. Following the paper by Patel and Goodby [2], we used the commercial mixture Chisso 2004 which has a quoted cone angle of 44° at a temperature of 25°C. In this paper we present results, namely spatial resolution, contrast ratio, optical sensitivity and switching speed of the pixellated OASLM using the twisted ferroelectric liquid crystal effect.

[1] L.W.K. Yim, A.B. Davey and A.R.L. Travis, to be appeared in Journal of Ferroelectrics (April, 1996).

[2] J.S. Patel and J.W. Goodby, Opt. Eng., 26, 373 (1987).

ACTIVE COLOR LCDs, N.R.Posledovich, Institute of Applied Physics Problems, Kurchatova 7, Minsk, 220064, Rep. Belarus

Investigations of physical properties of liquid crystals allowed to create inexpensive, simple in manufacturing, full color LCD. The change of color (black, red, green, blue, white) in these LCDs occurs at the expense of electrooptical effects in the liquid crystal (active color LCD) without use of color filters or special backlight.

D1P.51

NONPOLAROID LSDs, N.R.Posledovich, Institute of Applied Physics Problems, Kurchatova 7, Minsk, 220064, Rep. Belarus

The special processing of a glass plates' surface with electrodes leads to the formation of sufficiently homogeneous confokal texture in a mixture of the optically active smectic liquid crystals. Depending on the properties of the mixture the realization of two stable states is possible: transversal and longitudinal stripe texture of a domain. An intermediate texture obtained by cooling of the sample is also possible when the transversal stripe texture is formed in the beginning. The mechanical or electrical affect results in the reorientation of the transversal texture in the longitudinal. These textures are not oriented and an intensive scattering of light occurs on them. Changing the optical properties of such confokal domain in a electrical field has allowed to create LCDs without polaroids.

D1P.52

MONOCLINIC SYMMETRY IN FERROELECTRIC LIQUID CRYSTALS AND THE IMPLICATIONS FOR DEVICES, <u>I.C. Jones</u>, and C.V. Brown, Defence Research Agency (DRA), St. Andrews Rd., Malvern, Worcs. WR14 3PS, UK.

With the realisation that the dielectric biaxiality of smectic C and smectic C\* liquid crystals plays a dominant role in the AC electric field behaviour [1] and that it leads to a minimum in the response time of ferroelectric liquid crystal devices [2], the importance of accurate determination of the three biaxial permittivities became an important part of material design for applications. Various methods have been suggested [3] but all of the literature measurements assume that the dielectric cone angle is equivalent to the optical cone angle. Tilted smectic phases have monoclinic symmetry and the physical properties in the plane perpendicular to the C2 symmetry axis disperse. In the present work, four measurement geometries are used to extract the three biaxial permittivities and the dielectric cone angle. The results are shown to have profound implications for device performance.

- [1] J.C. Jones, E.P. Raynes, M.J. Towler and J.R. Sambles, Mol. Cryst. Liq. Cryst. Lett., 199, 277 (1991).
- [2] J.C. Jones, M.J. Towler and E.P. Raynes, Ferroelectrics, 121, 91 (1991).
- [3] J.C. Jones and E.P. Raynes, Liq. Cryst., 11, 199 (1992). F. Gouda, et al, Phys. Rev A, 46, 951 (1992)



SUPPRESSION OF ELECTRIC FIELD-INDUCED INSTABILITIES IN CHIRAL SMECTICS CROSSLINKED BY A POLYMER NETWORK, M.Mitoy\*, H.Ishii, G.Andersson, L.Komitov, S.T.Lagerwall, P.Sixou\*, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden, \*Laboratoire de Physique de la Matiére Condensée (UA CNRS 190), Parc Valrose, F-06108 Nice Cedex 2, France.

Field-induced rotational instabilities may occur in chiral smectic liquid crystals subjected to an alternating electric field with an asymmetric addressing wave form [1,2]. The initial smectic layer alignment is disorder and finally transformed into a chaotic structure. The phenomenon of non-stable surface alignment is especially disturbing when driving smectic A\* cells at very high speed and may be fatal for certain applications. We show that these disturbances can be suppressed by UV polymerization of a cholesteric photo-crosslinkable material dispersed to a few percent in the smectic liquid crystal with hardly any deteriorating effects on the electro-optic performance. Polymerization was performed in samples being in the A\* phase, in the C\* phase and in the isotropic phase. The influence of the polymeric network on the FLC material's electro-optic properties is presented for each case (tilt of optic axis, response time, polarization). In addition to stabilizing the smectic layer order, the polymer network raises considerably the temperature stability of the liquid crystalline order.

# D1P.54

STUDY OF POLYMER NETWORK FERROELECTRIC LIQUID CRYSTAL DEVICE'S ANTI-SEISMIC PROPERTY, Weisong Zhao, Ruipeng Sun, Yanqing Tian, Ximin Huang, Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, P.R.China

Surface stabilized ferroelectric liquid crystal (SSFLC) panels and polymer network ferroelectric liquid crystal (PNFLC) panels were prepared at the same condition. And we investigated the anti-seismic property of them in two ways. One is stress test in which we put variable weight on the panel, and the other is strike test in which we drop the iron bead at variable height. The result of the experiment shows that PNFLC panels have much better anti-seismic property compared with SSFLC. Restoration test was made in all kinds of the destroyed panels. At last we discussed the mechanism of PNFLC anti-seismic property.

[ 1 ] N. VAKITA, T. UEMURA, H. OHNISHI, H. MIZUNO and H. YAMAZOE, Ferroelectrics, 149, 229 (1993).

#### D1P.55

A NETWORK STABILISED FERROELECTRIC LIQUID CRYSTAL SYSTEM

<u>Ian Mason</u>, J.Clifford Jones and Damien McDonnell Liquid Crystal research division, Defence Research Agency St Andrews Road, Gt Malvern, Worcestershire, UK.

The surface stabilised ferroelectric liquid crystal (SSFLC) display suffers from a degree of shock sensitivity<sup>1</sup>. A blow or knock on such a display has a detrimental effect upon the alignment of the liquid crystal and thus reduces the display performance. This sensitivity will limit the potential of these devices in many environments. We have investigated effect of the addition of a stabilising polymeric network to the SSFLC device as a means of making these displays more rugged<sup>2</sup>.

Our work has involved the fabrication of several experimental devices with differing network densities. Studies have compared the stability our ruggedised devices with non ruggedised versions. Work has been carried out to investigate the consequences of such networks on display multiplexing performance.

In this presentation we outline the effects we have observed and discuss the possibilities which exist for such stabilised systems used within displays.

[1] J. Pris, R. Blinc et al. 14th Int. Liq. Cryst. Conf. Pisa Poster C-P89

[2] R. Hikmet, H. Boots and M. Michielsen, Liquid Crystals Vol. 19 No. 1 1995

INFLUENCE OF CONFINEMENT ON DIELECTRIC PROPERTIES OF FERROELECTRIC LIQUID CRTYSTAL, H. Ding, F.M. Aliev<sup>1</sup>, J.R. Kelly, and G.P.Sinha<sup>1</sup>, Physics Department and Liquid Crystal Institute, Kent State University, Kent, Oh 44242 and Materials Research Center, University of Puerto Rico, San Juan, PR<sup>1</sup>

We performed dielectric spectroscopic investigations of ferroelectric liquid crystal (FLC) confined in porous media: porous silicate glass matrices with average pore sizes of 1000 Å (volume fraction of pores 40%) and 100 Å (27%). In bulk SmC\* phase there are two dielectrically active modes: the Goldstone mode (characteristic frequency  $f \sim 10$  Hz) and the soft mode ( $f \sim 10^5$  Hz). The spatial confinement and the existence of a highly developed interphase have the strong influence on dielectric properties of FLC. We found that at temperatures about 50 °C below bulk melting temperature T =76 °C the dielectric behavior of confined FLC is very different from the behavior which is expected for solid state: the dielectric modes were not frozen in both porous matrices and we observed three relaxational processes with relaxation times  $\tau_1 \sim 10^{-1}$  s,  $\tau_2 \sim 10^{-4}$  s and  $\tau_3 \sim 10^{-6}$  s. In 1000 Å pores  $\tau_3$  increases when temperature approaches T=55 °C from below and above but it does not diverge like in conventional critical slowing down. This behavior is dependent on pore size. In 100 Å the third process is faster than in 1000 Å pores, the peak in  $\tau_3$  is broader and appears at T=50 °C. Dielectric properties of confined FLC can not be decribed by Landau theory of bulk FLC.

D1P.57

ELECTRO-OPTIC RESPONSES OF POLYMER DISPERSED FERROELECTRIC LIQUID CRYSTALS\*, K.K.Raina, Jasjit K. Ahuja and Arvind Kumar Thapar Institute of Engg. & Technology, P.Box 32, Patiala 147 001. INDIA.

We have investigated electrical and electro-optical properties of polymer dispersed ferroelectric liquid crystal (PDFLC) thin films. These films were prepared by mixing Norland optical adhesive (NOA 65) as a prepolymer and the ferroelectric liquid crystal mixture SCE 4 (Merck Ltd. U.K.) in different wt. ratios above the isotropic temperature. The mixture was phase separated by using UV polymerisation phase separation process [1-2]. The tilt angle, switching time and dielectric constant measurements have been carried out on the PDFLC samples of varying thickness over wide range of temperature. The results have been compared with the dispersion free ferroelectric thin films.

[1] H.S.Kitzerow, Liquid Cryst. 16, 1 (1994)

[2] H. Molsen and H.S. Kitzerow, J. Appl. Phys., 75, 710 (1994)

**D1P.58** 

CONTROL OF ELECTRO-OPTIC MODULATION IN POLYMER DISPERSED-FERROELECTRIC LIQUID CRYSTALS, <u>Jae-Hoon Kim</u>, Kyehun Lee, and Sin-Doo Lee\*, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

We report on the layer alignment and the associated electro-optic (EO) effect in polymer-dispersed ferroelectric liquid crystals (PDFLCS) [1]. It was found that an optimum size of FLC droplets in the polymer matrix exists for producing the best quality of the alignment of both molecules and smectic layers. For FLC materials possessing a long helical pitch in the smectic C\* (Sm C\*) phase, the EO modulation strongly depends on the droplet size as well as its shape in a restricted geometry while for short pitch materials, it is predominantly governed by the intrinsic helical structure in the Sm C\* state. The competition between the elastic distortions and surface interactions at the polymer/FLC interface is also discussed.

[1] K. Lee, S-W. Suh, and S.-D. Lee, Appl. Phys. Lett. 64, 718 (1994).

<sup>\*</sup> supported by AICTE Grant 166 / R&D / Chemical.

<sup>\*</sup>Supported in part by Advanced Materials Chemistry Research Center through Korea University.



NEW  $\alpha,\beta$ -UNSATURATED KETONES 1R,4R-MENTHANE-3-ONE DERIVATIVES AS CHIRAL DOPANTS IN FERROELECTRIC LC SYSTEMS, A.P.Fedoryako, <u>L.A.Kutulya</u>, E.V.Popova, V.V.Vaschenko, Institute for Single Crystals, Academy of Sciences of Ukraine, 60 Lenin Ave., Kharkov 310001,Ukraine

The ferroelectric properties of LC systems consisting of the achiral ester C smectogenics and the first synthesized nonmesogenic chiral dopants (CD) of  $\alpha,\beta$ -unsaturated ketone homologous series are studied. The high values of

$$O = 1, 4-6$$

the spontaneous polarization  $P_s$  is caused by the significant dipole magnitude of the carbonyl group which is rigidly attached the chiral fragment and orthogonal to the long molecular axis [1]. It is found that the minimal values of the ratio  $\gamma_{\varphi}/P_s$  which determines the electrooptic switching times in the Klark-Lagerwall effect are reached at the relatively small concentrations of CD (7.5-9.5 mol.%). The rotational viscosity values ( $\gamma_{\varphi}$ = 0.3-0.15 Poise over optimum concentration range) decreases

with the alkyl radical elongation. The strong effect of the CD structure on the  $\theta_c$  smectic tilt angle (15–39°) is observed. This effect allowed to obtain the  $\theta_c$  optimal values using the several CD for the given composition.

[1] L.Kutulya, N.Pivnenko, I.Nemchenok, et al., Zh. Obshch.Khim. (Russian). 57, 397 (1987).

#### D1P.60

THE OSCILLATION PROCESSES IN FERROELECTRIC LIQUID CRYSTALS, A.P. Fedoryako, E.V. Popova, Institute for Single Crystals, Academy of Sciences of Ukraine, 60 Lenin Ave., 310001, Kharkov, Ukraine.

Oscillation processes have been revealed by the reversible polarization study in ferroelectric liquid crystals (FLC). The polarization vector oscillation frequency was found to be 3-5 kHz. The oscillation process was shown to be independent of the "backflow" appearance. The investigations were carried out on the eutectic mixture of achiral smectic C LC with the 2-arylidene-p-menthan-3-ones [1] or optically active esters of 4,4"-terphenyldicarboxylic acid [2] used as chiral dopants. The oscillation process parameters have been investigated in dependence on the spiral wave vector value and the viscosity of mixtures. The oscillation amplitude dependence on wave vector value has been found. The weak dependence of oscillation frequency on the rotational viscosity has been detected as well.

- [1] L. Kutulya, I. Nemchenok, T. Handrimailova, Kristallografia (Russian) 35, 1234 (1990).
- [2] A.Andreev, N.Chernova, I.Kompanets, at al., Optical Information Processing, 212/SPIE, 2051,212 (1993).

#### D1P.61

LOW FREQUENCY RELAXATIONS IN A FERROELECTRIC LIQUID CRYSTAL WITH THE HELIX TWIST INVERSION, V. Novotná, M. Glogarová, H. Sverenyák, and A.M. Bubnov, Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18040 Prague 8, Czech Republic.

Dielectric and electrooptic dispersions have been studied in the frequency range from 10Hz to 1MHz in a liquid crystal with 2-alkoxypropionate chiral group, which exhibits the SmC\* phase in the temperature range from 124 to 70°C and the helix twist inversion at about 110°C. The dispersions reveal two modes, one is the well known Goldstone mode and the other (thickness mode) is connected with the fluctuations of the twist along the sample thickness, which is impossed by the polar surface anchoring in the SmC\* phase [1]. The modes can be distinguished due to spontaneous unwinding of the helix near the inversion temperature. The relaxation frequencies and dielectric strengths of both modes exhibit strong thickness dependences and anomalies around the inversion temperature due to anomalous temperature dependence of the helix pitch. The results are discussed on the basis of the elastic free energy taking into account the real structure of ferroelectric liquid crystals in finite samples.

[1] M. Glogarová, H. Sverenyák, J. Holakovský, H.T. Nguyen, and C. Destrade, Mol. Cryst. Liq. Cryst. 263, 245 (1994).

P-180

DIELECTRIC PROPERTIES OF A HOMOLOGOUS SERIES OF A CHIRAL ALKYL 4-N-ALKANOYLOXYBIPHENYL-4'-CARBOXYLATE, WHICH SHOWS SIGN-INVERSION OF THE SPONTANEOUS POLARIZATION T. F"utterer, G. Heppke, J.-M. Hollidt, Iwan N. Stranski Institute, Technische Universit"at Berlin, Sekr. ER 11, Stra"se des 17. Juni 135, D-10623 Berlin

As reported earlier [1,2], the homologous series of alkyl 4-n-alkanoyloxybiphenyl-4'-carboxylate shows sign-inversion of the spontanous polarization in the ferroelectric SmC\* phase. In order to describe this phenomenon, a change of the molecular conformation [1,3] was assumed. Recently a new model was proposed [4], which accounts for the observable sign inversion of the macroscopic polarization by special anchoring conditions arising from charges accumulated at the electrodes. In this contribution we report on the first comprehensive dielectric and electro-optical studies in order to clarify the origin of the sign inversion.

- [1] J.W. Goodby et al., Ferroelectrics, 147, 291 304, (1993)
- [2] R. Eidenschink, F. Gouda, S.T. Lagerwall, Ferroelectrics, 84, 167 181, (1988)
- [3] S. Saito et al., Ferroelectrics, 147, 367 394, (1993)
- [4] L. M. Blinov, L. A. Bresnev, D. Demus, 5th International conference on ferroelectric liquid crystals, lecture T14 New sight on the polarization sign inversion in ferroelectric liquid crystals, Cambridge (1995)

D1P.63

MEASUREMENT OF THE ELASTIC CONSTANTS AND EFFECTIVE SURFACE ANCHORING ENERGY FOR A FERROELECTRIC LIQUID CRYSTAL, C.V. Brown, P.E. Dunn and J.C. Jones, Liquid Crystal Group, Defence Research Agency, St. Anderws Road, Great Malvern, Worcs WR14 3PS, U.K.

Optical extinction angle spectra of the ferroelectric material 4-nonyl-2',3'-difluoro-4"-heptyl terphenyl in the surface stabilised geometry have been measured as a function of the applied ac electric field and temperature. The results were fitted by a model which assumes uniformly tilted incompressible layers either side of an infinitely anchored chevroned interface. The model uses the free energy expression of Leslie *et. al.* [1] to calculate the liquid crystal c-director profile through the cell and Jones matrices to calculate the optical properties. With no applied voltage this gives a structure which is very close to a triangular director profile [2]. An applied ac voltage couples to the dielectric biaxiality causing director reorientation in the bulk of the cell. At increased voltages an excellent fit is obtained by allowing movement of the director at the surfaces of the cell by using a finite surface anchoring energy in the model. The fits give the values of the c-director bend (B<sub>1</sub>) and splay (B<sub>2</sub>) elastic constants and the effective surface anchoring energy as a function of temperature.

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- [2] M.H. Anderson, J.C. Jones, E.P. Raynes and M.J. Towler, Liquid Crystals 10 (3), 439 (1991)

D1P.64

INVESTIGATION OF THE BIASED ROTATION DEGREE OF CHIRAL MOLECULE AROUND ITS MOLECULAR AXIS IN THE FERRO ELECTRIC LIQUID CRYSTAL MIXTURE, Z. Raszewski, J. Rutkowska, J. Kędzierski, P. Perkowski, W. Piecek, J. Zieliński, J. Żmija, R. Dąbrowski, Military University of Technology, 00-908 Warsaw, Poland.

Spontaneous polarization ( $P_S$ ), tilt angle ( $\theta$ ), helical pitch ( $\lambda$ ), dielectric ( $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$ ) and densytometric ( $\rho$ ) characteristics versus temperature and concentration of chiral dopand have been measured for FLC mixture. On the base of computer modelling the molecular dipole moment ( $\mu$ ), transverse ( $\alpha_t$ ) and longitudinal ( $\alpha_l$ ) molecular polarizabilities as well as angles ( $\gamma$  and  $\beta_0$ ) between the vector  $\mu$  and main long n or short 1 molecular axes of inertia have been calculated. Knowing the molecular parameters  $\mu$ ,  $\alpha_l$ ,  $\alpha_t$ ,  $\gamma$ ,  $\beta_0$  and state parameters  $\theta$ ,  $\lambda$  spontaneous polarization  $P_S$  has been calculated as the vector sum of the components of molecular dipole moment  $\mu_{\perp}$  perpendicular to the tilt direction. To do it the Zeks [1] rotational potential modified by us [2] has been used. After comparing spontaneous polarization  $P_S$  taken from experiment and obtained from theoretical approximation the biased rotation parameter  $\eta$  has been calculated.

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FIELD-INDUCED BIAXIALITY IN THE REFRACTIVE INDEX OF CHIRAL SMECTIC A LIQUID CRYSTALS, J. R. Lindle, F. J. Bartoli, S. R. Flom, A. Harter, B. R. Ratna, R. Shashidhar, Naval Research Lab, Washington, DC, 20375.

Chiral smectic A liquid crystals are of considerable interest for applications requiring fast analog electrooptic modulation. In the present work, the transmission of a homogeneously aligned chiral smectic A liquid crystal, placed between crossed and parallel polarizers, is measured as a function of polarization angle for a series of applied voltages. The experimental results exhibit a pronounced field-dependent birefringence, providing the first clear evidence for field-induced biaxiality in the refractive index in these systems. In the absence of an electric field, the chiral smectic A phase is normally considered to be uniaxial with the long molecular axis aligned with the smectic layer normal and the molecules free to rotate about their long axis. With an applied electric field, this axial symmetry is broken. The angle  $\beta$  between the two optical axes is found to vary linearly with the optical tilt angle, consistent with the above interpretation.

**D2P.02** 

OBSERVATION OF TWO TYPES OF MODULATIONS IN CHIRAL SMECTIC-A MATERIALS WITH LARGE ELECTROCLINIC COEFFICIENTS. <u>H. Li</u>, G. Rubin, J.V. Selinger, R. Shashidhar and B. R. Ratna, Code 6900, Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, Washington DC 20375, USA

We have investigated the effect of the electric field and sample thickness on planar oriented chiral smectic A liquid crystals. Under a low frequency electric field, we observe two modulations of the smectic layers with wavelengths that are independent of the field strength. The first one scales as twice the sample thickness and is attributed to the periodic, out-of plane layer deformation caused by the reduced layer thickness on the application of E-field [1]. The second modulation, which is rotated with respect to the first, is found to be independent of the sample thickness. The effect of the proximity of the smectic C\* phase on this modulation will be presented.

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**D2P.03** 

EFFECT OF ELECTRIC FIELD ON THE LAYER PROFILE OF A ONE-DIMENSIONALLY DISTORTED SMECTIC-A LIQUID CRYSTAL, R.E. Geer, S.

Sprunt\*, J.V. Selinger, J. Naciri, B. Ratna & R. Shashidhar, Code 6900, Naval Research Laboratory, Washington D.C. 20375,\*Department of Physics, Kent State University, Kent, Ohio 44242.

Chiral smectic-A materials with large electroclinic coefficients exhibit a static one-dimensional (1-d) modulation of the layers in a direction perpendicular to the layer normal. Using the x-ray diffraction technique, the variation of the layer profile of the 1-d distorted layer has been mapped in real-space as a function of the electric field. The layer profile is found to be triangular at high fields and sinusoidal at low fields and is compared with the model of Pavel and Glagorova [1]. These results, supported by the optical diffraction data, constitute the first qualitative mapping of the layer profile of a smectic-A under a varying electric field.

[1] J. Pavel & M. Glagorova, Liq. Cryst. 9, 87 (1991).



ELECTROOPTIC CHARACTERISTICS OF FREE-STANDING SMECTIC ULTRA-THIN FILM, Sadahito Uto, Hideyo Ohtsuki, Masanori Ozaki and Katsumi Yoshino, Department of Electronic Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, Japan

Electrooptic effects in a free-standing ultra-thin (60~500 Å) film of ferroelectric liquid crystal have been studied. The threshold field of the electrooptic effect in the free-standing film is negligible compared with that in a sandwich cell. The response time of the electrooptic effect in the free-standing film is much shorter than that in a sandwich cell. These effects have been interpreted in terms of the strong influence of the glass surface of the sandwich cell [1]. The response time becomes shorter with increasing electric field and especially at a certain threshold of electric field it changes in step-wise by three orders of magnitude. The response time of the faster kind of response which appears in the higher field region is about one thousand times faster than the slower kind of response at lower fields.

[1] S. Uto, H. Ohtsuki, M. Terayama, M. Ozaki and K. Yoshino, Jpn. J. Appl. Phys. 35, (1996) in Press.

# D2P.05

INFRARED SPECTRA OF LIQUID CRYSTAL MIXTURES AND ANALYSIS BY GAUSSIAN RADIAL BASIS FUNCTIONS TECHNIQUES, K. M. Yin, School of Technology, Kent State University, Ohio, USA, and <u>Takashi Kayano</u>, Department of Computer Information Science, Shimane University, Matsue, Japan.

We have reported the classification of infrared spectra of binary liquid mixtures of 4-n-nonyl-4'-cyanobiphenyl (9CB) and 4-n-pentylphenyl-trans-4'-pentylcyclohexane-1-carboxylate (5H5) using Back Propagation networks (BPNs)[1]. For the analysis of large sets of data, such as in the cases of infrared spectra of mixtures of 9CB and 5H5, the radial basis functions networks (GRBFNs) are better than the BPNs. The input neurons represent selected spectral intensities in the range of 1000 - 4000 wave numbers/cm. The output neurons represents the concentrations of the mixtures, the phases (isotropic, nematic and smectic) at the experimental temperatures. The GRBFNs correctly predict the phases. The predicted compositions of the mixtures agree with the experimental values within 5% error.

[1] Khin M. Yin and Takashi Kayano, Proceedings of the EXPERSYS-94 Expert Systems Applications & Artificial Intelligence, Volume 1, 673 (1994).

#### **D2P.06**

THE TEMPERATURE-MAGNETIC FIELD PHASE DIAGRAM OF A CHOLESTERIC LIQUID CRYSTAL, Rina Seidin and David Mukamel, Weizmann Institute of Science, 76100 Rehovot, Israel, and David W. Allender\*, Kent State University, Kent, Ohio, 44242, USA.

The phase diagram of a bulk cholesteric liquid crystal in a magnetic field perpendicular to the pitch axis is studied. This is an example of a system which exhibits a phase transition between modulated and homogeneous states. The region of the homogeneous state contains a first order line of transitions ending in a critical point. The line separates homogeneous states of strong and weak orientational order. The modulated to homogeneous transition may be either continuous and described by condensation of solitons having a repulsive interaction, or first order. The temperature-magnetic field phase diagram is found to be strongly dependent on the intrinsic chirality. For large chirality, the transition changes its character from first order to continuous via a multicritical point. This point becomes a critical end point for small chirality.

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REFLECTION CHARACTERISTICS OF BISTABLE CHOLESTERIC LIQUID CRYSTALS, B. Taheri, D. Davis, A. Khan, and J.W. Doane, Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

It is known that cholesteric liquid crystals exhibit bistability at zero field; that is, the helical axis can orient in different directions. This distribution can have a great effect on the optical properties of the reflected light. We present the results of a systematic study of the optical properties of polymer and surface stabilized cholesteric cells. The helical distribution induced by different stabilization techniques are measured and related to the optical properties using coupled wave analysis. The results indicate that the distribution function is sensitive to the stabilization method. Optical properties, however, appear to be more sensitive to the induced distribution than to the stabilization mechanism.

\* This project is sponsored by ALCOM

D2P.08

CHOLESTERIC SMART REFLECTORS, Ching-Chao Chang, Franklin Lonberg and Robert B. Meyer, The Martin Fisher School of Physics, Brandeis University, Waltham, MA 02254-9110, U.S.A.

We report the demonstration of cholesteric smart reflectors, consisting of a cholesteric liquid crystal with temperature sensitive helix pitch, in combination with a light absorbing dye. Light entering the liquid crystal is absorbed by the dye, generating heat which raises the temperature of the liquid crystal. The resulting change in the pitch length of the cholesteric causes an increase in its reflectivity, reducing the intensity of light that can be absorbed by the dye. This negative feedback stabilizes the reflector for a given light intensity. The smart reflector thus achieves a reflectivity which increases with increasing intensity of incident light. We report on two configurations of the device, with both experimental measurements and mathematical model of the system.

D2P.09

SIGN REVERSAL OF THE FLEXOELECTRIC ANISOTROPY IN CHOLESTERICS P. Rudquist, L. Komitov, S.T.Lagerwall, Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

In cholesterics, an applied electric field perpendicular to the helix axis may induce a periodic splay-bend deformation and thus a flexoelectric polarization. The magnitude and the sign of the polarization can be shown to depend on the magnitude and the sign of the flexoelectric "anisotropy"  $\Delta e = e_s - e_b$ , where  $e_s$  and  $e_b$  are the flexoelectric coefficients for splay and bend respespectively. The sign of  $\Delta e$  can be investigated by measuring the linear flexoelectric response in the cholesteric. Performing such measurements, as a function of temperature, we have found several materials, for which  $e_s - e_b$  changes sign with temperature. One case is a multicomponent mixture with a constant pitch in a wide temperature range; two cases are pure substances, one of them known also for a conformational change in the tilted smectic phase (sign reversal of the polarization).



# THE FLEXOELECTRO-OPTIC EFFECT IN CHOLESTERICS

Per Rudquist

Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

The flexoelectric effect in short-pitch cholesterics can be used for a fast electrooptic modulating device in which the angular deflection is a linear function of the applied field. First demonstrated by Patel and Meyer in 1987, the phenomenon has attracted new interest in recent years. A certain materials development, as well as progress in experiment and theory, now permits field-induced tilt of more than 22.5° giving a continuous grey-scale effect with possible 100% degree of modulation of transmitted light.

Our experimental and theoretical results on this flexoelectro-optic effect are presented and we discuss the influence on the effect from material parameters as the flexoelectric "anisotropy"  $\Delta e = e_s - e_b$ , the dielectric anisotropy  $\Delta e$  and the elastic constants  $K_1, K_2$  and  $K_3$  and make a comparison with other linear electrooptic effects in liquid crystals.

# D2P.11

THE EFFECT OF CHIRAL DOPANTS ON THE TGB STATES IN LC SYSTEMS BASED ON THE ACHIRAL SMECTIC C, N.L.Kramarenko, V.I.Kulishov\*, L.A.Kutulya, G.P.Semenkova, V.P.Seminozhenko, N.I.Shkolnikova, Institute for Single Crystals, Academy of Sciences of Ukraine, 60 Lenin Ave, Kharkov 310001 Ukraine; \*Institute of Physics, Academy of Sciences of Ukraine, 46 pr. Nauki, Kiev 252028, Ukraine.

The phase diagrams of some LC systems consisting of the achiral smectic C matrix and different chiral dopants (CD) with the induced TGB phases are studied. As the achiral SmC matrix the eutectic mixture of the 4-hexyloxyphenyl-4'-octyloxy- and 4-octyloxyphenyl-4'-hexyloxybenzoates (7:3) I is used. The compounds II (mesogenic) and III (nonmesogenic) are employed as CD. In all phase diagrams at critical point where the SmC\*, TGB and SmA phases coexist the TGB region is divided into two zones disposed between the N\* and SmC\* or the N\* and SmA phases respectively. The different macrostructure of two TGB states (TGB<sub>C</sub> and TGB<sub>A</sub>) is discussed.

R-(
$$\sim$$
)-CH=N- $\stackrel{\star}{C}$ H-CH<sub>2</sub>- $\stackrel{\star}{C}$ H-CH<sub>2</sub>- $\stackrel{\star}{C}$ HI(a-c) m = 2; R = C<sub>n</sub>H<sub>2n+1</sub>, n = 7(a), 9(b),11(c) HI m = 1; R = OC<sub>8</sub>H<sub>17</sub>

The CD structure influences significantly on the TGB region topology. As the alkyl radical length of CD II molecules increases the  $TGB_A$  zone decreases and disappears completely at n=11. The most concentration extension of the TGB region is observed for the system I — III. The  $\theta_c$  decrease with the CD concentration growth is important factor of the  $TGB_C$  state formation. On the example of the system I — IIb in which the ratio of the optically active and racemic forms is varied at their constant summary concentration the direct evidences of the dependence of the TGB range from the helical twist are obtained.

# D2P.12

INVESTIGATIONS ON THE FLEXOELECTRIC AND ELECTROCLINIC EFFECT IN THE N\* PHASE, I Dierking\*, P. Rudquist, L. Komitov, S. T. Lagerwall, B. Stebler, \*Institut für Physikalische Chemie der Technischen Universität Clausthal, D-38678 Clausthal-Zellerfeld, Germany; Liquid Crystal Group, Department of Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden

Measurements of the temperature and electric field dependence of flexoelectro-optic and electroclinic effects in the N\* phase of four different absolute configurations of a compound with two chiral centres are presented. For the flexoelectro-optic response in samples with uniform lying helix texture, a field-induced deviation of the optic axis in the range of  $\phi$ < 10° is detected. The response is linear with the field and its temperature dependence essentially follows that of the pitch p. In one of the compounds, exhibiting a helix inversion, no change in the sign of flexoelectric anisotropy was found on passing the inversion point. In this compound, the electroclinic effect in the N\* phase around the inversion point (p =  $\infty$ ) was also investigated. The angular deflection was found to be linear with the field, being about 100 times smaller in magnitude than the maximum flexoelectric response in this substance, yet much faster.

FLEXOELECTRIC EFFECT IN HYBRID ALIGNED NEMATIC CELL STUDIED BY MEANS OF HALF-LEAKY GUIDED MODES. <u>P.Rudquist</u>, E.L.Wood, R.Stevens, L.Komitov, S.T.Lagerwall, J.R.Sambles,

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We have studied the flexoelectric effect in MBBA by means of the half leaky guided mode technique /1/ in a Hybrid Aligned Nematic (HAN) cell. Due to the elastic deformation of the director field a volume flexoelectric polarization is present and an electric field, applied perpendicularly to the flexoelectric deformation plane couples with the flexoelectric polarization to induce a twist of the structure. From the magnitude of the field-induced twist the bulk flexoelectric coefficient (e<sub>s</sub> - e<sub>b</sub>)/K is estimated. This method gives a more complete picture than optical microscopy of the influence of the electric field on the hybrid structure.

/1/ F.Yang, J.R.Sambles, J. Opt. Soc. Am, B, 10, 858-866 (1993)

D2P.14

THE ELECTRO-OPTICAL PROPERTIES USING THE FLEXOELECTRIC EFFECT IN NEMATIC CELLS, <u>T. Takahashi</u>, S. Hashidate, M. Kimura and T. Akahane, Dept. of Electrical Engineering, Nagaoka Univ. of Tech. 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan.

We investigated the flexoelectric effect of nematic liquid crystals with negative dielectric anisotropy in the HAN cell and the SPLAY cell for application to LCDs. The electric field is applied parallel to the substrate plane. Simulations were carried out theoretically by using the continuum theory for the field-induced deformation of director orientation and the electro-optical characteristics. The theoretical model includes the polar and azimuthal anchoring energy and the dielectric energy. In this model, the director reorientation is especially affected by the azimuthal anchoring energy when the electric field is applied to the cell. Some experimental results are shown.

- 1) I. Dozov, Ph. Martinot-Lagarde, and Durand, J. Physique Lett., 43, 365 (1982)
- 2) A.Derzhanski, A.G.Petrov and M.D.Mitov, J. Physique, 39, 273(1978)

D2P.15

INTRAMOLECULAR AND INTERMOLECULAR CHIRALITY TRANSFER IN THE FORMATION OF INDUCED CHOLESTERIC PHASES, <u>Hans-Georg Kuball</u>, Holger Brüning, Bernhard Weiß, Fachbereich Chemie, Universität Kaiserslautern, 67663 Kaiserslautern, Germany

For the description of pitch and sign of an induced cholesteric phase no universally valid relation between parameters of the structure and helical twisting power (HTP) can be formulated because for different structures various mechanisms with different weighting factors should be responsible for size and sign of the HTP. From our results one can try to piece the process of chiral induction into at least two steps [1] which can cause different effects for amino-anthrachinon compounds with one or several chiral centers: the intramolecular and intermolecular chirality transfer. Furthermore, TADDOLs have very large values for the HTP and are suitable to achieve large changes by small variation of their structure. A new additional mechanism for helix inversion by a variation of the principal axes of the order tensor, e.g. the orientation axis, with respect to the orientation of the chiral center via a special substitution has been found. Besides, it is shown that two identical chiral centers only will yield twice of the effect of one chiral center if the orientation axis of the system with respect to the "orientation" of the chiral center is the same.

[1] H.-G. Kuball, H. Brüning, Th. Müller, O. Türk, and A. Schönhofer, J. Mater. Chem., 5, 2167 (1995).



NMR DETERMINATION OF TENSOR ORDER PARAMETER IN CHOLESTERYL ESTERS LIQUID CRYSTAL PAHSES, I.V.Oleynikova, V.A.Andreev, Department of theoretical physics, Physics faculty, Kiev Shevchenko University, pr.Glushkov 6, 252127 Kiev, Ukraine.

The procedure of using the method of moments of NMR lines and the molecular configuration of protons in solid phase for determing the absolute value of order parameter S and the orientation of axes of order parameter tensor in the molecular system of coordinates in cholesteric and smectic phases of typical cholesteric liquid crystals (ChLC) is suggested. This procedure is used for determining the order parameter tensor for gomologous series of cholesteryl esters. The dependence of S on chain length is found. The proposed method can be used to estimate the concentration of two independent conformations of the molecule and the influence of translation diffusion of molecules along ChLC axis.

#### D2P.17

#### STEREOGLASSES WITH CHIRAL LC AND PDLC,

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Stereoglasses for PC monitors provide volume vision and reconstruction of virtual reality for educational, military, training and other purposes. We have studied parameters of varioous glasses with liquid crystal electrooptic shutters. Some of them contain polarizers (ferroelectric LC, 900 and 2700 twist). For this reason they have low transmittance and alternative light flux on each eye. It induces fatigueness of operator. We have tested also a series of various types of PDLC shutters. They are transparent in onstate (65-80%) and opaque in off-state. The switch time (1-7 ms) is sufficient for the stereoeffect. Main advantage of the stereoglasses is very weak variation of light flux on user's eye and absence of fatigueness.

#### **D2P.18**

LIQUID-CRYSTALLINE PROPERTIES OF CHOLESTERYL ESTERS DERIVED FROM COCONUT OIL, Leonorina G. Cada and Arnold Tamayo, Institute of Chemistry, University of the Philippines, Diliman, Quezon City, 1101, Philippines

Selective reflection properties of short pitch length cholesteric liquid crystals find applications in thermometry, thermal mapping, radiation sensing, decorative and novelty products. As in the case for electro-optic applications of liquid crystals, materials intended for practical use in thermochromic devices are invariably mixtures of several different compounds. Standard formulations are commercially available from which mixtures suitable for common device applications can be derived. These commercial formulations are however costly due to expensive synthetic methods. The study presented provides an alternative route to lower cost of production by utilizing inexpensive and readily available coconut oil and cholesterol as starting materials. Coconut oil is a rich source of fatty acids. Esterification with cholesterol yields a mixture of coco-fatty acid cholesteryl esters. The resulting mixture show liquid crystallinity at a temperature range of 54-78 degrees centigrade. The textures observed under the polarizing microscope are typically cholesteric and smectic. Properties of several formulations based on the prepared esters are presented.

TWISTED GRAIN BOUNDARY PHASE IN THE BINARY MIXTURE OF NEMATIC AND CHOLESTERYL COMPOUNDS.

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\*Department of Chemistry, University of Southampton, S017, IBJ, UK. The binary mixture of cholesteryl nonanoate and 4,4'-hexvloxy azoxy benzene (HOB) exhibit a very interesting meso phases like blue phase, twisted grain boundary (TGB) phase, induced smectic A, smectic C and smectic B phases at different temperatures when the mixture is cooled from isotropic phase. The existence of TGB phase is confirmed by reflection, X-ray and optical microscopic studies. The mixtures with concentration 20 to 35% of CN exhibit TGB phase at higher temperature. DSC and Birefringence studies are also been carried out. The optical anisotropy of cholesteric is estimated. Numerous interesting optical textures phase also illustrated. R.Pindak: 1) Goodbye.J.W; M.A.Waugh; E.Chin: and S.M.Stein; J.S.Patel Nature 337, 449(1989).

**D2P.20** 

A TWO-MODE CHOLESTERIC ELECTRO-OPTIC DEVICE, <u>L.Komitov</u>, S.T.Lagerwall, P.Rudquist, B.Stebler, Department of Physics, Chalmers University of Technology, S-41296 Göteborg, Sweden

In short-pitch cholesteric liquid crystals the helix axis takes on the properties of a macroscopic optic axis. Such materials with ULH (uniform lying helix) texture may exhibit a field-induced tilt of the optic axis due to flexoelectricity /1/. The tilt is a linear function of the applied field at least for small fields. If the dielectric anisotropy of the material has a non zero value, the dielectric torques will give rise to deviation of the electro-optic response from the linear behaviour, due to deformation or partially unwinding of the helix, on increasing the field /2/. At sufficient high fields, however, a transition from cholesteric to nematic takes place and the response becomes purely quadratic. Hence, in cholesterics aligned in ULH texture, two operational modes can be distinguished - flexoelectric and dielectric.

We present a new cholesteric device operating in both flexoelectric and dielectric mode. A remarkable feature of this device is that it can work in a wide temperature range as a linear modulator or as a light shutter, depending on the applied voltage.

[1] J.S.Patel, R.B.Meyer, Phys. Rev. Lett., 58, 1538 (1987)

[2] P.Rudquist, L.Komitov, S.T.Lagerwall, Phys. Rev.E, 50, 5020 (1994)

D2P.21

FIRST INVESTIGATION OF THE PHASE BEHAVIOUR AND ELECTROOPTICAL PROPERTIES OF A HOMOLOGOUS SERIES OF CHIRAL DISCOTIC DIBENZOPYRENE DERIVATIVES, G. Heppke, D. Krüerke, D. Lötzsch, M. Müller and H. Sawade, Iwan N. Stranski Institute, Technische Universität Berlin, Sekr. ER 11, Straße des 17. Juni 135, D-10623 Berlin

Electrooptical effects in columnar mesophases of chiral discotic molecules were found only a few years ago [1]. Since then, little has been added to that knowledge. We have systematically varied the molecular structure of chiral dibenzopyrene derivatives and investigated their macroscopic physical properties such as phase behaviour and electrooptical properties.

$$\begin{array}{c} R \\ R \\ R \end{array} \qquad R = \begin{array}{c} O \\ O \\ C_n \\ H_{2n+1} \end{array}$$

[1] H. Bock, W. Helfrich, Liq. Cryst. 12 (4) 697-703 (1992)

OPTICAL ACTIVITY OF SHORT PITCH CHIRAL LIQUID CRYSTALS

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 $N^*$  and  $S_c^*$  LC exhibit rotatory power for light propagating along the helix axis, which decreases as  $(p/\lambda)^3$  for  $p \ll \lambda$ , where p is the helix pitch and  $\lambda$  is the light wavelength. Recently, it has been shown that in the same limit helical shaped structures can display optical activity also for light propagating orthogonally to the helix axis, but now with a strength decreasing as  $p/\lambda$  [1]. Such structures can be modelled as optically active homogeneous media. Analytic expressions have been found for the gyrotropy parameter g of the equivalent homogeneous media [2]. For  $S_c^*$  LC g depends on the tilt angle  $\alpha$  as  $\sin^2(2\alpha)$ , and is zero for  $N^*$ . However, it has been theoretically shown (P. G.) that also flexoelectrically distorted cholesterics display optical activity and that the gyrotropy parameter again decreases with p as  $p/\lambda$ . The properties described above will be tested by experiments and by numerical computations. Some preliminary computations show that the homogeneous model for the undistorted structures retains its validity well beyond the limit  $p \ll \lambda$ .

[1] P. Allia et al., J. Phys. II France, 4 333 (1994); [2] C. Oldano and M. Rajteri, submitted for publication.

# D2P.23

SOME ASPECTS OF TEMPERATURE DEPENDENCE OF STEP OF INDUCED CHOLESTERICS, Z. Mikityuk, A. Fechan, V. Zhelih, O. Vozniak, State University "Lvivska Politechnika", Bandera Str., 12, Lviv, Ukraine, 290646.

The step of helix induced by an optical active dopant in a nematic matrix is one of important parameters of induced cholesterics. This parameter determines the volt-contrast, time and hysteresis properties of cholesteric-nematic phase transition. This dedicated to studies of a temperature behavior of helix induced cholesterics on the base of cianobipheniles exycianobipheniles. As an optical active depants the cholesterine esters and non-liquid crystal substances are used. On the base obtained results the mathematical model of temperature behavior of pitch was elaborated and the pitch empiric dependence concentration of components of nematic matrix and optical active dopants with a temperature was fixed.

# D2P.24

#### NOVEL FEATURES IN BLUE PHASE KOSSEL DIAGRAMS

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The complete determination of any periodic structure using Bragg diffraction involves three measurements: the layer spacings from the Bragg diffraction angles; the amplitudes of the Fourier components of the structure from the scattering intensities; and the relative phases of these Fourier components from the phase information in the diffracted light. These three types of information about the structure become progressively harder to obtain. The final piece of the puzzle, the so called 'phase problem', is the hardest to solve since it requires interferometry to determine the phase of the diffracted light.

In this work a solution of the phase problem is presented which exploits the interference of coherent light diffracted from different Bragg planes in the blue phases. The experimental geometry is simple to achieve using the Kossel diagram technique. Results are presented illustrating novel features at the crossing points of the diffracted Kossel lines which are modelled using a simple theory and shown to depend strongly on the relative phases of the Bragg planes in the sample. The results are found to contradict the model of BPII commonly illustrated in the literature.

SHEAR-INDUCED PIEZOELECTRIC EFFECTS IN CHOLESTERIC ELASTOMER GELS, Ching-Chao Chang and Robert B. Meyer, The Martin Fisher School of Physics, Brandeis University, Waltham, MA 02254-9110, U.S.A.

We report a piezoelectric effect in cholesteric liquid crystalline elastomer gels. When we apply a shear stress to a cholesteric elastomer gel in the direction perpendicular to its helical axis, a polarization can be induced in the direction perpendicular to both the stress and the helix. This experimental observation agrees with the theory proposed by Pelcovits and Meyer [1].

[1] R. A. Pelcovits and R. B. Meyer, J. Phys. II France 5, 877 (1995).

**D2P.26** 

SUB 100 NANOSECOND PRETILTED PLANAR-TO-HOMEOTROPIC NEMATIC ELECTRO-OPTIC SWITCHING UNDER HIGH ELECTRIC FIELD STEPS, <u>Hidehiko Takanashi</u>, Joseph E. Maclennan\*, and Noel A. Clark\*, Sony Corporation, Research Center, Yokohama, 240, Japan, \*Department of Physics, University of Colorado, Boulder, CO, 80309, USA.

Simple nematic elasto-hydrodynamic theory predicts the risetime  $\tau$  for electric field induced molecular reorientation to scale with applied field E as  $\tau \sim 1/E^2$ . We report here the first results of a research program directed toward probing the breakdown of this relationship in the large-E/small- $\tau$  limit. We employ miniature indium-tin oxide on glass Electro-Optic(EO) cells which, because of their small area and RC time constant, enable the application of fast, high voltage steps (10 nsec, 1000V) to the LC. Molecular reorientation is probed optically with 632.8nm light by placing the cell and a compensating wedge between crossed polarizers and monitoring the transmission, T. Results reported here were obtained in a 2  $\mu$ m thick nematic 5CB cell with 15° pretilted planar alignment at E = 0. The wedge adjusted to cancel the birefringence of this initial state, i.e. giving T = 0 at E = 0. At high voltage the EO response is bimodal, with T rising rapidly in a fast transient to  $\sim$  0.7, and then much more slowly to  $\sim$  1. The risetimes of the fast portion of the response are as short as 40 nanoseconds have been observed in response to a 400V step, with the later slow rise to T = 1 requiring several microseconds. At lower fields the risetimes of the fast transient agree well with a model of bulk switching with a uniform director (surface and flow effects are shown to be unimportant) employing the known dielectric anisotropy and viscosity of 5CB. Risetimes become slower than the model values for at the highest E. The origin of the slower switching process is unknown.

#Work supported by Sony Corporation, NSF MRG Grant 92-24168, and ARO Grant DAAH04-93-G-0164.

D2P.28

CIRCULARLY POLARIZED EMISSION FROM VITRIFIED CHIRAL NEMATIC FILMS\*, H. Shi, B.M. Conger, and S.H. Chen\*\*, Center for Optoelectronics and Imaging; A. Schmid, Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623; T. Tsutsui, Department of Materials Science and Technology, Kyushu University, Kasuga, Fukuoka 816, Japan

The theory of circularly polarized fluorescence (CPF) from a chiral nematic liquid crystalline film was first attempted by Pollmann et al (1976). Under the condition that the emission wavelength is much less than the selective reflection wavelength, analytical solutions were obtained for polarization efficiency in two limiting cases. In their theory light absorption was assumed to occur isotropically, and the effect of film thickness vanished as a result. We have completed a general theory, which has been shown to be capable of recovering the two limiting cases. To formulate a more realistic comprehensive theory, both CD and selective reflection should be included. Our preliminary results suggest the feasibility of this refined approach. It should permit one to investigate the effect of thickness on CPF, which is critical to the determination of the minimum thickness needed to take full advantage of the potential of a chiral nematic film for producing CPF. Relevant experimental data will also be presented to validate the theoretical prediction.

\*Supported by MITI (Japan), NSF Grant CTS-9500737, and DOE Grant DE-FC03-92SF19460

INVESTIGATION OF DOMAIN INSTABILITY IN THE FOUR DOMAIN TWISTED NEMATIC CONFIGURATIONS, J. Chen, P.J. Bos, N.D. Kim, J. Li and J. Crow, Liquid Crystal Institute and Department of Physics, Kent State University, Kent, OH, 44242, USA.

For the multi-domain TN displays, the display with four-domain structure gives an optimum view angle characteristics and gray scale performance. However, the domain instability of the four domain TN configurations in the operating state is a big obstacle for its practical application. In this paper, the origins of the instability in the all proposed four domain TN configurations are investigated. We evaluate the critical conditions for the domain stability using our simple model. The consequences of the model have been tested by experiments. The preventions for domain instability are also suggested.

## **D2P.30**

INTRODUCTION TO THE PHYSICS OF FERRONEMATIC LIQUID CRYSTALS Yu. Raikher, Institute of Continuum Media Mechanics, Urals Branch of RAS, Perm, 614061, Russia

A theory describing physical properties of suspensions of single-domain erroparticles (mean size  $L\sim100$  nm) in liquid-crystalline (nematic) matrices is presented. The systems in question, more known as ferronematics, are interesting from a number of viewpoints; in particular, because their magneto-optical susceptibility is orders of magnitude greater than that of usual liquid crystals. The principles of the classic theory by Brochard and de Gennes are discussed. It was the first to show a route from mesoscopic problems (a single particle in a LC environment) towards the behavior of a collection of grains and finally - to the continuum theory on the scale >>L. However, the range of applicability of the B-d-G model is rather limited due to the assumption that the infinitely strong anchoring of the liquid crystal on the particle surfaces. Excluding this postulate, we have developed a generalised theory, thus covering the cases of finite anchoring energies. Retaining the main merits of its predecessor, our model became more capable and allowed a noncontradictory quantitative explanation of the existing train of data on thermotropic ferronematics. From the achieved level of understanding, the prospects of development are discussed; in particular - description of magneto-dynamics of ferronematics.

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#### D2P.31

# A NEW OPTICAL MEASUREMENT METHOD FOR THE DETERMINATION OF LC PRETILT ANGLE IN FULL RANGE OF 0-90 DEGREES

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Pretilt alignment of liquid crystal remarkably influences on the electro-optical properties of liquid crystal display (LCDs). Hence, it is necessary to accurately measure the pretilt angle in full range of 0°-90°. At present, the following methods have been reported: crystal rotation method[1], capacitance measurement method[1], etc. Among them, the crystal rotation method is most widely used because precise measurement are rapidly obtained. This method, however, can not be applied for the cell with any pretilt angle in the range of about  $16^{\circ}$ - $60^{\circ}$ ; for a pretilt angle in this range, there is no corresponding incident angle to render a extremum retardation because of the refraction of light at boundary surface. Moreover, in case of thin LC cells about less than  $10\,\mu$  m, the pretilt angle measured by the crystal rotation can contain a significant error. To solve these problems, we developed a new method called "Polarizer Rotation Method" in which the pretilt angle can be obtained by selecting a polarization direction of incident light to render the excitation of either ordinary or extraordinary wave inside the LC cell. This method is useful for the accurate measurement of pretilts (0°-90°) without the restriction of measurable range and dependence of cell gap thickness. Eventually, we verify the validity of the Polarizer Rotation Method by a calculation of theory and an experiment.

PROPERTIES OF AMORPHOUS NEMATIC LIQUID CRYSTAL DISPLAYS Betty Kerlleñevich, Universidad Tecnológica Nacional, 8000 Bahía Blanca, Argentina

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The alignment of the liquid crystal molecules in the nematic displays was thus far obtained by rubbing of the glass substrates. Toko and al.<sup>[1]</sup> have proposed a method of fabrication of "amorphous LCD" without rubbing by using a mixture of the nematic and a chiral dopant (smectic S811), injected in the isotropic phase into the cell of a thickness d. The cell is then cooled down to the room temperature, the cooling rate affecting the created amorphous textures. We have investigated such a cell which behaves as a twisted cell of thickness d with a twist angle  $\theta = 2\pi d/p$ , p being the pitch of the mixture nematic-smectic. If d/p = 1/4,  $\theta$  is equal to  $\pi/2$ . The curves giving the optical transmission T vs the voltages applied to the cells are plotted for various mixtures of some nematics and the smectic; they show that the transmissions decrease for voltages of the order of 2 volts and cancel at about 3 volts for  $d \equiv 5 \mu m$ .

[1] Y. Toko, T. Sugiyama and K. Katoh, J.Appl. Phys. 74 (1993) 2071.

D2P.33

HOMEOTROPIC TO TWISTED PLANAR TRANSITION IN NEMATIC LIQUID CRYSTALS WITH NEGATIVE DIELECTRIC ANISOTROPY, Seong-Woo Suh and Sin-Doo Lee\*, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

A homeotropic to twisted planar (HTP) structural transition is demonstrated in a homeotropically aligned nematic liquid crystal (NLC) with negative dielectric anisotropy. This HTP transition results in a novel electro-optic effect useful for extremely high contrast, wide viewing, and achromatic display applications. The twist in the field on-state on approaching the HTP transition can be controlled by both an external twist imposed by the rubbing process and the amount of a chiral dopant introduced into NLCs. This HTP architecture is found to be a promising candidate for use in the active addressing scheme. The role of the surface anchoring and molecular chirality on the HTP transition is also discussed.

\*Supported in part by RCDAMP through Pusan National University.

D2P.34

DIVERGENCE ELASTICITY OF A NEMATIC CELL WITH HIGH PRETILT ANGLE, <u>D. Subacius<sup>1</sup></u>, V.M. Pergamenshchik<sup>1,3</sup>, and O.D. Lavrentovich<sup>1,2</sup>, <sup>1</sup>Liquid Crystal Institute and <sup>2</sup>Chemical Physics Program, Kent State University, Kent, OH 44242, USA, <sup>3</sup>Institute of Physics, National Academy of Sciences, Kyyiv, Ukraine.

S.Faetti (Mol. Cryst. Liq. Cryst. 241, 131 (1994)) suggested a test of validity of different theoretical approaches to the  $K_{I3}$  problem. According to the so-called first-order elastic theory,  $K_{I3}$  term causes spontaneous long-range deformations when a magnetic field is applied along uniformly tilted director. These deformations can be detected in optical phase retardation measurements with distinctive non-monotonous behavior of phase retardation when magnetic field increases. In contrast, the second-order theory predicts  $K_{I3}$ -induced molecular scale deformations even when there is no field. Our experiments on phase retardation as a function of the magnetic field for cells with high pretilt angle lead to the conclusion that either (a)  $|K_{13}| \le 0.3$ pN for nematic 5CB or (b) the formal application of the first-order theory (without high order terms) to the uniform director geometry is not correct.

The work was supported by NSF ALCOM Center Grant DMR-20147.



REFRACTIVE INDEX OF NEMATIC LIQUID CRYSTALS IN THE SUBMILLIMETER WAVE REGION, <u>T.Nose</u> and S.Sato, Dept. of Electr. & Electronic Eng., Akita Univ. Akita, 010, JAPAN, K.Mizuno and J.Bae, Res. Inst. of Electr. Comm., Tohoku Univ., Sendai, 980-77, JAPAN T.Nozokido, Photodynamics Res. Center, The Inst. of Phys. & Chem. Res., Sendai, 980, JAPAN

Most efforts in the research works on optical properties of liquid crystal materials are concentrated on a visible region, because of the large demand from display applications. However, liquid crystals are also very attractive materials from a view point of applications to various optical devices for other wavelength regions. Since the refractive index is indispensable data for the use of electrooptical effects in liquid crystals, it is very important work to measure the refractive index in unknown wavelength regions. We have proposed a determination method of refractive indices in a submillimeter wave region ( $\lambda = 118,215,435 \,\mu$  m) by using a submillimeter wave laser and a characteristic matrix solution. The refractive indices of cyanobiphenyl compounds for ordinary and extraordinary rays are measured. The index value is treated as a complex and the loss parameter is also estimated. The refractive index is a little larger than that in the visible region but the birefringence is comparable with that in the visible region. Loss level is larger by two orders of magnitude than that of quartz which has an excellent transparency in the submillimeter wave region, but the total loss of the liquid crystal cell is sufficiently low.

### D2P.36

STEADY STATE CURRENT IN NEMATIC LIQUID CRYSTALS, S. Murakami, H. Naito, M. Okuda, and A. Sugimura\*, Department of Physics and Electronics, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 593, Japan, \*Department of Information Systems Engineering, Osaka Sangyo University, Nakagaito, Daito, Osaka 574, Japan.

A steady state current flowing in nematic liquid crystals (NLCs) has been studied for NLC cells with configuration of ITO/5CB/ITO and ITO/PI/5CB/PI/ITO, where PI is the polyimide aligning layer. For the cell with configuration of ITO/5CB/ITO, a plot of the logarithm of the steady state current vs the square root of applied voltage is characterized by two straight lines with different slopes, which would be due to the Schottky effect and the Poole-Frenkel effect at lower and higher applied voltages, respectively. For the cell with configuration of ITO/PI/5CB/PI/ITO, on the other hand, the plot of the logarithm of the steady state current vs the square root of applied voltage is essentially characterized by a single straight line. Furthermore, the current is four orders of magnitude smaller than that of the ITO/5CB/ITO cell at 4 V. This is due to the fact that the PIs block the charge injection from the electrodes.

#### D2P.37

THE MULTIPLEXIBILITY AND THE ELECTROOPTICAL PARAMETERS OF LC MIXTURES CONTAINING 2-[4-(4'-CYANO-3-HALOGENPHENYLOXYCARBONYL)-3-HALOGENPHENYL]-1,3,2-DIOXABORINANES,V.I.Lapanik\*,V.S.Bezborodov,Institute of Applied Physics Problems, 220064, Minsk, Belarus, \*Present adress: Samsung Display Devices Co. Ltd., R&D Center, 575, Shin-Dong, Paldal-Gu,Suwon City,Kyungki-Do,Korea.442-390.

The analysis of the electrooptic parameters of LC mixtures containing 2-[4-(4'-cyano-3-halogenphenyloxy-carbonyl)-3-halogenphenyl]-1,3,2-dioxaborinanes with different lateral substituents have shown that compounds with Cl-lateral substitution more strongly decrease the threshold voltage and increase the steepness of the electrooptical curve than compounds containing fluoro atom. This can be explained as the increased dipole moment, as well as the increased dielectric anisotropy, especially for the parallel component .Presence of two lateral substituents leads to further increasing dielectric anisotropy and deacreasing threshold voltage, especially for the compounds containing fluoro atom in ortho position to cyano group. The investigations have shown that not only the dielectric, electrooptic and dynamic parameters, but also multiplexibility of the mixtures are defined by the concentration of the dioxaborinanes. It have been found that these compounds, especially 15% weight of the difluoroderivatives in nonpolar base mixture may be used for the preparation of high multiplexive mixtures (1:128).

EFFECT OF THE IN-PLANE BROKEN SYMMETRY ON ELECTRO-OPTIC PROPERTIES OF NEMATIC LIQUID CRYSTALS, Youngjin Kim<sup>†</sup>, Seong-Woo Suh, and Sin-Doo Lee\*, Physics Department, Sogang University, CPO Box 1142, Seoul, Korea.

A finite degree of the twist, breaking the in-plane symmetry, is predicted to produce a polar electrooptic (EO) effect in nematic liquid crystals (NLCs). This prediction is experimentally confirmed
by making a finte twist incorporated into a planar cell with symmetric interfaces. Similar effect of
the out-of-plane broken symmetry has been reported previously [1]. The magnitude of the polar
effect is essentially dictated by the amount of the twist through the anchoring renormalization at
NLC/substrate interfaces. The physical origin comes primarily from the flexoelectricity present
in a deformed state of twisted NLCs.

[1] S.-D. Lee and J. S Patel, Phys. Rev. Lett. 65, 56 (1990). <sup>†</sup>On leave from Orion Electric Co., Korea.

D2P.39

ELECTRO-OPTICAL AND DIELECTRIC PROPERTIES OF NEMATIC TRIMERS, N.V. Tsvetkov, V.N. Tsvetkov, V.V. Zuev, Institute of Macromolecular Compounds of the Russian Academy of Sciences, Bolshoi pr. 31, St. Petersburg, 199004, Russia.

The method of orientational elastic deformations in electric fields was used to study electro-optical and dielectric properties of nematics of the trimer series (bis-(4-cyanobiphenyloxyalkaneoxy)biphenyls):

[1] V.N. Tsvetkov, N.V. Tsvetkov, S.A. Didenko, V.V. Zuev, Mol. Cryst. Liq. Cryst. Vol. 265, 341 (1995).

D2P.40

METASTABLE NEEL WALLS PARALLEL TO GLASS PLATES IN NEMATIC LIQUID CRYSTALS, J. M. Gilli, S. Thiberge, <u>C. Chevallard</u>, I.N.L.N., CNRS UMR 129, 1361 Rte des Lucioles, 06560, France; A. Buka, Research Institute for Solid State Physics, Hungarian Academy of Sciences, Pf. 49., 1525 Budapest, Hungary; L. Kramer, Physikalisches Institut Universitat Bayreuth, Postfach 10 12 51. D-8580 Bayreuth

We describe experimental properties of metastable domains with turn over of the director, observed with homeotropically anchored nematic or cholesteric liquid crystal sandwiched between parallel glass plates. This distorted situation stabilized by the application of a field parallel to the plates have been observed in the past in the neighborhood of nematic-air interface or in some studies of directional phase transformations at the N-I interface (1,2). The application of electric field perpendicular to the plates on positive  $\Delta \epsilon$  materials allows the thickness control of the reversal region in the bulk of the sample and the phase dynamics behavior of the director can be understood in the frame of a two dimensional model.

Moreover this experimental system gives us the opportunity of observing singular points defects in the bulk of the sample, with reversible transformations between them and looped singular lines (3) in the

particular case of flatened globules.

1) P.E. Cladis, W. van Saarloos, P. L. Finn, A. R. Kortan, Phys. Rev. Lett., 58, 222, 1987.

2)J. Bechhoefer, PHD THESIS, The University of Chicago, December 1988.

3) H. Mori, H. Nakanishi, J. of the Phys. Soc. of Japan, 57, 1281, 1988.



SURFACE TENSION MEASUREMENTS OF VARIOUS SMECTIC-A LIQUID CRYSTAL FILMS,\* P. Mach, S. Pankratz, S. Grantz, T. Stoebe, and C. C. Huang, Department of Physics, University of Minnesota, Mpls., MN 55455, USA.

Employing a novel experimental technique, we have measured the surface tension of sixteen different liquid crystal compounds in smectic-A free-standing films. Within our experimental resolution of about  $\pm 1.5\%$ , the surface tension for a given compound is found to be independent of the film thickness for films thinner than about 100 layers [1]. Our new results reveal that four different groups of materials with distinct values of surface tension can be identified. The most plausible explanation for our observation is that the packing of the molecular cores will affect the packing of the tails of the molecules. The tail arrangement in the immediate vicinity of the film/vapor interface is mainly responsible for the film surface tension. Further experimental effort is being made to address the role of the molecular packing on the measured surface tension.

[1] P. Mach, et al., J. Phys. II France 5, 217 (1995). \* Supported in part by NSF Grant DMR 93-00781

## D2P.43

LIGHT-INDUCED SURFACE EFFECTS IN DOPED NEMATIC LIQUID CRYSTALS, Yu.Reznikov<sup>1)</sup>, F.Simoni<sup>2)</sup>, O. Francescangeli<sup>2)</sup>, S.Slussarenko<sup>1)</sup>, D.Voloshchenko<sup>1)</sup>, <sup>1)</sup>Institute of Physics, Nat. Acad. Sci., Prosp. Nauki 46, Kyiv 252022 UKRAINE, <sup>2)</sup>Department of Material Sciences, University of Ancona, Via Brecce Bianche, I-60131, Ancona, ITALY

Control of the orientational state of LCs by light action on aligning surfaces is of great interest for high density optical storage, information processing and new photoaligning techniques[1,2]. The new mechanisms of such control are presented. We found that the illumination of azo-containing LC with polarized light can induce a high speed director reorientation on the isotropic aligning surface. Typical times of the director "sliding" over the aligning surface are of the order of 1ms. Light-induced surface memory effects may be also observed in the system [3]. A light induced homogeneous alignment on the isotropic surfaces, stable with time and temperature, can be produced at a high concentration of the dopant. This effect is characterised by extremely small light exciting intensities (5 10-2 W/cm<sup>2</sup>). The results obtained were applied to record both stationary and dynamic holograms with a 7µm spatial resolution. A strong selfgaining of stationary holograms was observed. The surface memory effects were applied to record both binary and grey scale images.

[1] W. Gibbons et al., Nature, 351, 49 (1991); [2] T. Marusii, Yu.Reznikov, Mol.Mat. 3, 161 (1993); [3] D.Voloshchenko et al., Jap Journ. Appl. Phys., 34, 566 (1995).

## D2P.44

IN-LINE FIBER POLARIZATION SELECTOR AND INTENSITY MODULATOR, Tien-Jung Chen, J. M. Hsu\*, and Shu-Hsia Chen\*, Department of Electronics, Chienhsin College of Technology & Commerce, Chungli, Taiwan. \*Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, 300, R.O.C.

Fiber components utilizing the combination of liquid crystals and fibers are attractive due to the easy handling of liquid crystals. Moreover, the optical characteristics of liquid crystals, highly birefringent and readily altered by external electric field, make the fiber components based on liquid crystals versatile. A single mode fiber enclosed with planar aligned liquid crystals is reported. The fiber was etched to about 10 micrometers in diameter to approach the fiber core [1]. The output light was exercised through the evanescent field coupling between the fiber and surrounding liquid crystals [2]. The optical polarization state and intensity level are changed with liquid crystal molecules reoriented electrically. Once the electrical field is switched on, the perpendicular polarization suffers tunneling loss while the horizontal polarization remains no propagation loss. Therefore, the electrically controlled polarization selection and intensity modulation can be achieved.

[1] Z. H. Wang, D. G. Wang, and S. R. Seshadri, Microwave and Optical Technology Letters. 4, 491 (1991).

[2] C. Veilleux, J. Lapierre, and J. Bures, Opt. Lett. 11, 733 (1986).

OPTICAL PROPERTIES OF HOMEOTROPICAL ALIGNED LIQUID CRYSTAL MICROLENS A. Gwozdarev, G. E. Nevskaya, Novosibirsk State Technical University, Novosibirsk, Russia

A orientation of liquid crystal molecules at nonuniform electric field caused nonuniform spatial distribution of refractive index for extraordinary rays. This effect can be used to create optical devices with variable parameters. The optical properties of the homeotropical aligned liquid crystal cell with asymmetrical construction of electrodes have been researched. Holes with diameters equiled to 200, 400, 600, 800 µm were produced in one of electrodes by means of photolithography. The nonuniform radial symmetrical electric field caused the radial symmetrical distribution of refractive index for extraordinary ray at holes region. This structure possesses the diverging lens properties. Focal distanse - and phase retardation profile-voltage dependencies have been investigated by means of polarization microscope. The focal distance was a few millimeters and changed with voltage. Researching showed that the microlenses with ratio of hole diameter to the cell thickness L/d in the range from 5 to 10 possess best optical properties.

**D2P.46** 

VISUALIZATION OF DIRECTOR DISTRIBUTION FROM THE CROSS-SECTIONAL IMAGE USING A DYE DOPED UV CURED LIQUID CRYSTAL CELL, Shin Masuda\*, Toshiaki Nose and Susumu Sato, Dept. of Electrical and Electronic Engineering, Akita University,

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We have proposed and demonstrated a novel observation method to investigate the molecular orientation states in a cross section of the LC cells using a UV curable LC material.[1] Director distribution states of continuous molecular orientation and structures of disclination lines are clearly observed optically from the cross-sectional images of LC cells. Moreover, a complicated texture of the cholesteric in a wedge shaped LC cell have also been revealed. In this study, director distribution states in a cross section of the cured LC cells; that is, homogeneous, TN and bend cells are observed using a polarization microscope, and their director distributions are elucidated from the distribution of the transmission light intensity through the cured LC specimens using a dye doped UV curable LC material.

[1] S. Masuda, T. Nose and S. Sato: Jpn. J. Appl. Phys., 34, L1055(1995); Proc. of Asia Display '95,147 (1995)

**D2P.47** 

FIRST ELECTRIC CONDUCTION WITH HIGH HOLE MOBILITY IN SMECTIC A PHASE OF A CALAMITIC LIQUID CRYSTAL, M. Funahashi and J. Hanna\*, Laboratory of Imaging Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

In mesophase, carrier transport is expected to be superior to isotropic phase because of its molecular alignment, and also to polycrystal state due to lack of deep traps at grain boundaries. But only ionic conduction has been observed in calamitic systems although high hole mobility was reported in discotic columnar phase [1]. We synthesized photoconductive liquid crystal, 2-(4-heptyloxyphenyl)-6-dodecylthiobenzothiazole, which exhibited SmA phase between 90 °C and 100 °C, and showed larger photocurrent on the basis of hole transport in SmA phase under steady state illumination of UV light. Hole mobility was measured with Time-of-Flight technique, indicating that it was  $6x10^{-3}$  cm<sup>2</sup>/Vs in SmA phase which is six times larger than Dh phase of hexaalkoxytriphenylene [1], and  $6x10^{-5}$  cm<sup>2</sup>/Vs in isotropic phase. It is interesting that high carrier mobility can be realized in more disordered SmA phase than Dh phase.

[1]D. Adam et al., Phys. Rev. Lett., 70, 457 (1993); Nature, 371, 141 (1994).



ELASTIC CONSTANTS OF A SMECTIC-C LIQUID CRYSTAL.

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The elastic constants of a smectic-C liquid crystal exhibiting positive dielectric anisotropy have been determined via a study of the Freedericks transition in both flat and wedged shaped devices. Such experiments were first proposed by Leslie et al [1] for very specific device geometries and layer structures within the device. In this work the actual layer structure adopted by the material under investigation was determined using small angle x-ray scattering and further time resolved x-ray experiments were employed to examine the layer deformations on application of an electric field. The Freedericks transition of the smectic-C material and the deduced elastic constants are discussed with respect to the geometry of the layers within the device.

1. F Leslie et al, Mol. Cryst. & Liq. Cryst. 198, 443-454, (1991), T Carrlson et al, Liquid Crystals 9(5), 661-678, (1991); T Carrlson et al, Liquid Crystals 11(1), 49-61, (1992).

### D2P.49

ANALYSIS OF INFRARED SPECTRA OF LIQUID CRYSTAL MIXTURES BY NEURAL NETWORKS METHODS, K. M. Yin, School of Technology, Kent State University, Ohio, USA, and Takashi Kayano, Department of Computer Information Science, Shimane University, Matsue, Japan.

We have used neural network approach to the classification of infrared spectra of binary liquid mixtures of 4-n-nonyl-4'-cyanobiphenyl (9CB) and 4-n-pentylphenyl-trans-4'-pentylcyclohexane-1-carboxylate (5H5). We built the neural networks, using nonlinear back propagation algorithm (BPN). The input neurons represent selected spectral intensities in the range of 1000 - 4000 wave numbers/cm. The output neurons represents the concentrations of the mixtures, the phases ( isotropic, nematic and smectic) at the experimental temperatures. In the unsupervised learning mode, the networks correctly classify the liquid crystal phases [1]. In the supervised learning mode, the trained neural networks correctly predict the phases. The predicted compositions of the mixtures agree with the experimental values within 10% error. We applied a preprocessing technique and found that we have achieved better agreement.

[1] Khin M. Yin and Takashi Kayano, Proceedings of the EXPERSYS-94 Expert Systems Applications & Artificial Intelligence, Volume 1, 673 (1994).

#### **D2P.50**

LIQUID CRYSTAL BASED POLYMER FOR APPLICATIONS IN MMW MODULATION DEVICES, K. C. Lim, J. D. Margerum, A. M. Lackner and E. Sherman, Hughes Research Laboratories, Malibu, CA 90265; M.-S. Ho and B. M. Fung, Department of Chemistry, University of Oklahoma, Norman, OK 73019; W. B. Genetti and B. P. Grady, School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, OK 73019.

A liquid crystal monomer, which is the diacrylate of a bis phenyl diazene, was synthesized. It was polymerized in a magnetic field to form oriented polymers. The millimeter wave birefringence was measured for a polymeric rod with the macroscopic orientation perpendicular to its long axis, using a millimeter wave version of the Mach-Zehnder interferometer. It was found that  $\Delta n = 0.068$  at 30 GHz. Tensile testing was done to measure the mechanical proeperties of a plate with the orientation parallel to the long axis. The tensile modulus was found to be  $6.8 \times 10^8$  N/m<sup>2</sup>, about 4 times that of the same material without macroscopic orientation. The torsional rigidity modulus of the rod was also measured and found to be higher than  $10^7$  N/m<sup>4</sup>. Both the dielectric anisotropy and mechanical strength make the oriented polymer potentially suitable for application in a novel class of millimeter wave modulation devices.

INFRARED STUDY OF THE CHOLESTERYL n-ALKOXYBENZOATES MESOMORPHISM, Achil A.Yakubov, Faculty of Physics, Samarkand State University, University blvd.15, Samarkand, 703004, Uzbekistan.

The infrared absorption spectra in the range of 400-4000 cm<sup>-1</sup> for an eight gomologous of the cholesteryl n-alkoxybenzoates (one of the perspective cholesteric mesogenes) were measured in solid, liquid crystal and isotropic liquid phases. On this basis some conclusions concerning conformational and orientational disorder of molecules for different phases are discussed.

D2P.52

THE USE OF A HIGH SENSITIVE LIQUID CRYSTAL CELL FOR A REGISTRATION OF BREATH PARAMETERS, <u>A.S.Kashitsyn\*</u>, V.A.Balandin, S.V.Pasechnik and V.A.Tsvetkov, \*Ivanovo State University, PLLC, 153025, Ermak St., 39, Ivanovo, Moscow State Academy of Instrument and Informatics, 107846, Strominka 20, Moscow, Russia.

We have investigated the optical response of the liquid crystal cell to variations of an air pressure induced by a human breathing. The liquid crystal cell had two  $SnO_2$  coated glasses and two open sides to transfer a pressure difference to homeotropic layer of nematic liquid crystal with a positive anisotropy of dielectric permitivity. We used the electric voltage to change the sensitivity of the cell and the range of measurable pressure difference. We have also investigated the cells with a variable thickness of a nematic layer. Thus, we were able to register the pressure difference less then 1 Pa induced by a weak breathing.

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D2P.53

NUMERICAL CALCULATIONS OF ELECTROCLINIC EFFECT: EFFECT OF THE POLAR ANCHORING STRENGTH, M.Kimura, and T.Akahane, Department of Electrical Engineering, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka 1603, Nagaoka, Niigata 940-21, JAPAN.

The numerical simulation of the electroclinic effect in the smectic-A phase, which was based on the Landau-type free energy formula and included the surface anchoring effect, elastic effect and polarization electric field, has been proposed.[1] The numerical results demonstrated the remarkable effect of the non-polar and/or polar surface anchoring strength on the molecular reorientation. Here we discuss the influence of the polar surface anchoring strength on the molecular alignment just under the isotropic-smectic-A phase transition temperature. The difference between the rubbing direction and optical extinction angle (i. e. smectic layer normal) under the Iso.-SmA phase transition temperature can be explained by this simulation.

[1] M. Kimura, S. Okamoto, M. Yamada, T. Akahane and S. Kobayashi, Mol. Cryst. Liq. Cryst., 263, 189 (1995).



OPTICS OF SOME ABSORBING DEFECT LATTICES, G.S. Ranganath, N. Andal and K.A. Suresh, Raman Research Institute, Bangalore-560080, India.

We have studied optical reflection and diffraction in absorbing twist grain boundary smectics (TGBS) [1], lattices of asymmetric solitons [2] and solitons with oscillatory tails [3]. In these cases we have considered both uniformly and non-uniformly absorbing systems. Our studies show that the inherent asymmetry of individual solitons considerably affects the properties. For instance the reflection spectrum is different for light travelling in opposite directions. Further some novel features are found to be associated with the non-uniformly absorbing defect lattices. For example, a symmetric diffraction pattern is obtained for some non-uniformly absorbing TGBS unlike that of an uniformly absorbing TGBS which yields asymmetric diffraction pattern [1].

- [1] N. Andal and G.S. Ranganath J. Phys. II France 5 1193 (1995)
- [2] P.B. Sunilkumar and G.S. Ranganath J. Phys. II France 3 1497 (1993)
- [3] L. Lam, Solitons in liquid crystals Ed., L. Lam and J. Prost, Springer Verlag, (1991)

## D2P.55

INDUCED TWIST GRAIN BOUNDARY PHASE IN BINARY MIXTURES, Yuvaraj Sah, College of Military Engineering, PUNE - 31, INDIA.

We report induced Twist Grain Boundary (TGB) phase [1] formation in binary mixtures of n-nonyloxy-benzoic acid (NOBA) with Cholesteryl sterate (CS) and cholestesteryl caprylate (CC). The (NOBA/CS) mixture have been studied by optical microscopy, selective Bragg reflection and optical rotation. It was found that for X < 0.55 (X is the weight fraction of CS in NOBA) there is a direct Cholesteric-Smectic A transition. For X > 0.55 TGB phase occurs up to X = 0.9. The occurrence of the TGB phase was established by appearance of filament texture, (characteristic of the TGB phase), when the mixture is heated from homeotropic aligned Smectic A phase to cholesteric phase. The wavelength of the selective reflection and the rotation of the azimuth of the linear polarized light has been measured as the sample is cooled from the cholesteric phase to the TGB phase. The induced TGB phase is to be further investigated by DCS and the X-ray measurements.

[1] J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak and J.S. Patel, Nature, 337, 499(1989).

## **D2P.56**

SMECTIC C TWIST GRAIN BOUNDARY UNDER ELECTRIC FIELD, P. Barois, H.T. Nguyen, M. Nobili, M. Petit, Centre de Recherche Paul Pascal. Avenue A. Schweitzer, 33600 Pessac, France.

The Smectic C Twist Grain Boundary phase  $(TGB_C)$  is constituted of blocks of Smectic C with spontaneous polarization  $\mathbf{P}_S$ , stacked in an helical fashion around an axis x. In the early proposed  $TGB_C$  model  $\mathbf{P}_S$  was parallel to the pitch direction  $(\mathbf{P}_S \parallel \mathbf{x})$  [1]. Recent measurements of the  $TGB_C$  structure suggest that  $\mathbf{P}_S$  is orthogonal to the pitch axis  $(\mathbf{P}_S \perp \mathbf{x})$  [2]. In the later case,  $\mathbf{P}_S$  can be coupled to a transverse electric field  $\mathbf{E}_{ext}$  ( $\mathbf{E}_{ext} \perp \mathbf{x}$ ) to give an energy:  $\Delta F_i = -\int_{slab} \mathbf{P}_S \cdot \mathbf{E}_{ext} \ dV \propto -P_S E_{ext} s_i \cos \theta_i$ .  $\Delta F_i$  can be lowered either by rotating the  $i^{th}$  slab to bring the angle  $\theta_i$  between  $\mathbf{P}_S$  and  $\mathbf{E}_{ext}$  closer to  $\theta_i \approx 0 \mod 2\pi$  or/and by expanding the size  $s_i$  of the slabs having  $\theta_i \approx 0 \mod 2\pi$ . Experimentally, the  $TGB_C$  sample is prepared between two polymer coated and unidirectionally buffed glass plates. The  $TGB_C$  pitch is orthogonal to the plates. Two parallel gold wires are used as spacers and electrodes. The DC electric field is perpendicular to the pitch. The blocks orientation and thickness are measured by X-ray diffraction. The results support the assumption of transverse polarization. The electric field effect is also to vary the pitch length. Optical measurements of the helical pitch as function of the electric field amplitude are presented.

[1] S.R. Renn and T.C. Lubensky, Mol. Cryst. Liq. Cryst. 209, 349 (1991); [2] L. Navailles, R. Pindak, P. Barois and H.T. Nguyen, Phys. Rev. Lett. 74, 5224 (1995).

RELAXATION PHENOMENA IN N, SmA<sub>d</sub> AND N<sub>re</sub> PHASES, S.Wróbel\*, M.Brodzik\*, R.Dabrowski\*, B.Gestblom, W.Haase\*, S.Hiller\*, \*Inst. of Phys., Jagellonian Univ., Reymonta 4, 30-059 Kraków, Poland; "WAT, Warsaw, Poland; Inst. of Phys., Uppsala Univ., Sweden; Inst. of Phys. Chem., TH Darmstadt, Germany.

It has been discovered recently [1] that mixtures of highly polar nematics show an induced  $SmA_d$  and  $N_m$  phases. Dielectric properties and relaxation processes of two highly polar mixtures: two-component mixture (MIX I) and four-component mixture (MIX II), both composed of cyano-bi- and -ter-phenyls, have been studied by means of dielectric spectroscopy. In the case of MIX II the  $\varepsilon_N$  component shows a pronouced anomaly in incommensurate  $SmA_d$  phase due to dipole- dipole correlations. This anomaly is absent for MIX I which may mean that in this case one has to do here with  $SmA_1$  or  $SmA_2$  phase. The dielectric spectra measured for both mixtures consist of two well separated absorption peaks connected with two-phenyl and three-phenyl species. By fitting a sum of two Cole-Cole functions it was possible to calculate dielectric parameters of the relaxation processes observed. In both cases the dielectric relaxation time exhibits an Arrhenius type behavior with activation energy in the N phase higher than in  $SmA_d$  and  $N_m$ . In the high frequency range (from 1 MHz to 10 GHz) a broad spectrum has been found.

[1] M. Brodzik, R. Dabrowski, SPIE Proceedings, Vol. 2372, p.280 (1995). Supported by the KBN grant 2 P302 139 02 and Polish-German project BMBF (St.080.1).

D2P.58

NEMATIC-LIKE SMECTIC A ELASTIC RELAXATION AT SUB-λ SCALE, <u>I.Dozov</u>, Laboratoire de Physique des Solides, Universite Paris-Sud, bât. 510, 91405 Orsay Cedex, France

Usually, the smectic A is described with molecular director  $\mathbf{n}$  pointing everywhere rigorously along the layers normal  $\mathbf{q}$ . In that description a layer undulation with wave vector  $\mathbf{k}$  propagates along  $\mathbf{q}$  far away [1], at distance  $L\sim 1/(\lambda k^2)$ ,  $\lambda$  being the penetration length. Here we show that at  $k>1/\lambda$  the layer deformation relaxes with  $L\sim 1/k$ , as in a nematic. In this "nematic" regime the layers and the director distortions are decoupled,  $\mathbf{n}$  being controlled by the strong nematic elasticity. We discuss the importance of this "nematic" elastic relaxation around the defects or close to the surfaces. In particular, we demonstrate a large "nematic" contribution to the self energy of the edge dislocations. This effect explains the lower energy of the planar Melted Grain Boundary defects, recently observed [2] in bent smectic A, compared with a network of edge dislocations.

[1] G. Durand, C. R. Acad. Sci. Paris B, 275, 629 (1972); P.G. de Gennes, ibid., 275, 939 (1972).

[2] I.Dozov and G.Durand, Europhys. Lett., 28, 25 (1994).

D2P.59

MAGNETIC SUSCEPTIBILITY MEASUREMENTS IN TWO SYSTEMS SHOWING INDUCED SMECTIC A PHASE, N.K.Pradhan and R.Paul, Department of Physics, University of North Bengal, Siliguri, Pin-734430, West Bengal, India.

Magnetic susceptibilities of binary mixtures of 4-pentyl cyanobiphenyl (5CB) with 4-pentyl phenyl-4'-alkyloxy benzoate (alkyl = hexty or pentyl) have been measured using a modified Curie balance method [1]. Both these systems show induced smectic A phase and have been investigated previously by us using x-ray diffraction technique and refractive index measurements [2,3]. Magnetic susceptibilities over the entire mesomorphic range for different compositions were measured. Orientational order parameters (OOP) have been calculated from the magnetic susceptibility data and are in agreement with those obtained before from x-ray diffraction and refractive index studies. In particular, OOP in smectic A phase at a constant temperature (35 degree C) show a minimum at mole fraction of 5CB equal to 0.4 for both the systems in accordance with previous investigations [2,3].

[1] M.Mitra and R.Paul, Mol. cryst. Liq. Cryst., 148, 185(1987); [2] M.K.Das and R.Paul, Phase Trans., 46, 185(1994), ibid 48, 255(1994); [3] M.K.Das, R.Paul and D.A.Dunmur, Mol. Cryst. Liq. Cryst., 258, 239(1995). \*U.G.C. Teacher Fellow on leave from St. Joseph's College, Darjeeling, Pin-734104, West Bengal, India.



INFLUENCE OF RIGID CORE STRUCTURE ON THE ABILITY TO INDUCE THE SMECTIC A₄ PHASE IN POLAR SYSTEMS, M.Brodzik, R.Dąbrowski, Institute of Chemistry, Military University of Technology, 01-489 Warsaw, Poland.

The induction of smectic  $A_d$  phase in the form of a 'smectic island' in mixtures of nematic polar compounds was previously reported [1]. The influence of alkyl chain length and steric hindrances on the  $A_d$  phase induction was described [2,3]. Now the influence of rigid core structure on the induction phenomenon is presented. The phase diagrams of bicomponent systems containing as a first component four ring ester (1) and as a second component nematic cyanoderivatives (2) were studied.

$$H_{15}C_7 + \sum_{2} coo \left\{ \sum_{2} cN \right\}_{2}$$
 (1)  $H_{11}C_5 - Z - A - X - CN$  (2)

Z and X - polar bridge groups, A - different rings . In case of cyclohexylbenzene core the induction of an  $A_d$  phase is stronger then in the case of biphenyl core. The induction of  $A_d$  phase decreases when rings with heteroatoms (dioxane, pyridine, pyrimidine) or polar linking groups are introduced.

- [1] M.Brodzik, R.Dąbrowski, Liq.Cryst., 18, 61 (1995).
- [2] M.Brodzik, R.Dabrowski, Mol. Cryst. Liq. Cryst., 260, 361 (1995).
- [3] M.Brodzik, R.Dąbrowski, Liq. Cryst., 20, 99 (1996).

### D2P.61

TWIST GRAIN BOUNDARY IN CONFINED GEOMETRY, P. Barois, M. Nobili, M. Petit, Centre de Recherche Paul Pascal. Avenue A. Schweitzer, 33600 Pessac, France.

It was argued that the  $TGB_C$  (Smectic C Twist Grain Boundary phase) commensurability could be induced by the phase confinement [1]. To investigate this properties, we modelize the TGB [2] behavior in confined geometry. The TGB is kept between two parallel surfaces with strong planar anchoring. The anchoring of the nematic director and the confinement of the smectic slabs allow to apply a torque  $\tau$  and a pressure p on the slabs, respectively. Thus, a deviation  $\delta$  of the angle between the director of two adjacent slabs from the equilibrium value and a deviation  $\varepsilon$  of the slab thickness from the equilibrium block thickness are expected. We write the TGB elastic energy as function of  $\varepsilon$  and  $\delta$ . The TGB behavior depends on the coupling strength  $\beta$  between  $\varepsilon$  and  $\delta$ . We fix p=0 and  $\tau\neq 0$  and we vary  $\beta$ . For  $\beta=0$ , we find a constant  $\delta\neq 0$  and  $\varepsilon=0$  as expected. By increasing  $\beta$ , a distortion of  $\varepsilon$  and  $\delta$  appears, until that, for  $\beta\approx 1$ , the distortion is extended to the entire cell.  $\beta\approx 1$  is almost critical, in fact, for  $\beta>1$ , the TGB phase becomes unstable. The expected and measured X-ray diffracted signals are compared.

[1] Y. Galerne, Phys. Rev. Lett. 72, 1299 (1994); [2] S.R. Renn and T.C. Lubensky, Phys. Rev. A 38, 2132 (1988); J.W. Goodby, M.A. Waugh, S.M. Stein, E. Chin, R. Pindak and J.S. Patel, Nature (London) 337, 449 (1989); L. Navailles, P. Barois and H.T. Nguyen, Phys. Rev. Lett. 71, 545 (1993).

## D2P.62

TGB<sub>A</sub> AND TGB<sub>C</sub> MESOPHASES OF LIQUID CRYSTALLINE COMPOUNDS WITH TWO CHIRAL CENTRES, A. C. Ribeiro<sup>(1)</sup>, L. Oswald<sup>(2)</sup>, J. F. Nicoud<sup>(2)</sup>, D. Guillon<sup>(2)</sup>, Y. Galerne<sup>(2)</sup>, <sup>(1)</sup>Centro de Física da Matéria Condensada (U.L.), Av. Prof. Gama Pinto 2, 1699 Lisboa Codex, Portugal, <sup>(2)</sup>Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 23 Rue du Loess F-67037 Strasbourg, Cedex, France

The characterisation by X- ray, DSC and optical microscopy of two new liquid crystalline compounds is presented in this work. The compounds under consideration incorporate in the molecule carbon and sulphur chiral centres. While the chiral carbon is fixed in the R configuration the sulphur chiral centre may be either in the S or in the R configuration. For one of these two diastereomers it was detected the existence of a TGB<sub>A</sub> mesophase in a large temperature domain, while for the other one in a similar temperature range the existence of TGB<sub>A</sub> and TBG<sub>C</sub> mesophases was observed. For both diastereomers and in both mesophases it was possible to detect the coexistence of two different types of optical textures apparently associated with two different kinds of structural organisations. The pitch of the helix in the TGB mesophases was evaluated by means of optical reflection observations in samples exhibiting planar cholesteric textures. The induced phase transition TGB<sub>C</sub> - S<sub>C</sub>\* was obtained by the application of an AC electric field in a cell with surfaces treated for obtaining the SSFLC effect.

# DIELECTRIC RELAXATION STUDIES IN FRUSTRATED SMECTIC PHASES OF HIGHER HOMOLOGUES OF 50.m SERIES

D.M. Potukuchi, C.R. Prabhu and V.G.K.M. Pisipati, Centre for Liquid Crystal Research and Education, Nagariuma University, Nagariumanagar-522 510, India. Dielectric orientational relaxation studies (10³ to 10³ Hz.) are carried out in the higher homologues of 50 m. N-(p-n-pentyloxybeazalidine)p-n-alkylanilines with m = 12, 14 and 16 exhibiting [1] interdigitated smectic polymorphism. Nematic and smectic phases are characterised by Cole-Cole plots and their Debye type of relaxation mechanisms. Dipolar reorientation mechanism and the corresponding hindered degrees of freedom for the observed frustrated smectic-A is discussed in the wake of the reported orientational relaxations in the other mono-layer smectic phases. The Arrehenius plots drawn for the activation energies in nematic and smectic-A phases infer the distinct strengths of the smectic-A<sub>d</sub> potential barriers due to the interdigitation of the molecules.

[1] V.G.K.M.Pisipati and S.B.Rananavare, Liqd.Cryst., 13, 757 (1993).

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MESOMORPHISM OF NEW ISOMERIC OXADIAZOLES, L.A. Karamysheva<sup>1</sup>, S.I. Torgova<sup>1</sup>, A. Sparavigna<sup>2</sup> and A. Strigazzi<sup>2</sup>, <sup>1</sup> Organic Intermediates & Dyes Institute, Moscow, Russia, <sup>2</sup> Dipartimento di Fisica, Politecnico di Torino, Torino, Italia

Three new series of 2,5- disubstituted 1,3,4- and 3,5- disubstituted 1,2,4-oxadiazoles with reversed structures containing 4- alkylbiphenyl-, trans-4-alkylcyclohexylphenyl- (alkyl =  $n-C_3H_7$ ,  $n-C_5H_{11}$ ) and halophenyl- (Hal=ortho- or para- F,Cl,Br) have been synthesized. Mesophases types, transition temperatures and enthalpies were studied using the polarizing microscope in orthoscopic mode and by differential scanning calorimetry. The results are discussed in terms of molecular polarization accounting the structure of the molecule, the own dipole moment of the heterocyclic unit and the dipole moment of the polar halophenyl substituent. The last one is compared with the action of the nonpolar group (such as ortho-CH<sub>3</sub>).

D3P.02

SYNTHESIS AND CHARACTERISATION OF LONG CHAIN  $\alpha, \omega$ -BIS(4-CYANOBIPHENYL-4'-YLOXY)ALKANES, <u>F.I.Farrand</u>, and G.R.Luckhurst, Department of Chemistry, University of Southampton, Highfield, Southampton, SO17 1BJ, United Kingdom.

The transitional properties of liquid crystal dimers are of considerable interest because of the pronounced odd-even effect which they exhibit. These properties are found to depend on the length and parity of the flexible spacer as well as the geometry of the linking group between the spacer and the two anisometric groups. In previous studies [1], the first twelve members of the  $\alpha$ ,  $\omega$ -bis(4-cyanobiphenyl-4'-yloxy)alkanes have been synthesised and shown to exhibit this behaviour for both  $T_{NI}$  and the transitional entropy. The long chain homologues of this series from thirteen to twenty-one have now been prepared using various synthetic pathways. Characterisation of these dimers using optical microscopy and DSC has shown that the odd-even effect exhibited by  $T_{NI}$  is essentially removed as the chain length increases, in addition the entropy of transition is also attenuated for the longer spacers. This is in agreement with that predicted by the continuous rotational potential and not the RIS model [2].

- [1] Emsley, J.W., Luckhurst, G.R., Shilstone, G.N. 1984, Molec. Crystals. lia. Crystals Lett. 102, 223.
- [2] Ferrarini, A., Luckhurst, G.R., Nordio, P.L., 1995, Molec. Phys., 85, 131.

D3P.03

SYNTHESIS OF SEMI-PERFLUORINATED FLCS AND THE EFFECT OF FLUORINATION EXTENT ON MESOMORPHIC PROPERTIES, H. Liu\*, and H. Nohira, Department of Applied Chemistry, Saitama University, Urawa, Saitama, 338, Japan.

We have synthesized a series of semi-perfluorinated phenylbenzoate FLCs with a chiral (-)-2-fluoro-octanol endgroup and evaluated their mesomorphic properties[1]. It showed that fluorination of the achiral tail enhanced smectic A phase at low extent of fluorination and chiral smectic C phase at high extent of fluorination. We also synthesized a number of semi-perfluorinated phenylpyrimidine FLCs with a chiral (-)-2-fluoro-octanol endgroup and investigated their liquid crystalline properties. Also, the liquid crystalline properties of the FLC mixtures doped with semi-perfluorinated phenylpyrimidines were evaluated and the results will be reported on the day of the conference.

[1] H. Liu, and H. Nohira, Liquid Crystals, 1996(in press).

FORMATION OF COLUMNAR MESOPHASES BY CALAMITIC MOLECULES WITH HYDROPHILIC LATERAL GROUPS, J.-A. Schröter, R. Plehnert, R. Festag<sup>†</sup>, M. Wittenberg<sup>†</sup>, J. H. Wendorff<sup>†</sup>, and C. Tschierske\*, Institut für Organische Chemie der Universität Halle, Kurt-Mothes-Str.2, D-06120 Halle, and <sup>†</sup>Fachbereich Physikalische Chemie und wissenschaftliches Zentrum für Materialwissenschaften der Universität Marburg, Germany

We have synthesized and investigated novel p-terphenyl derivatives carrying large hydrophilic substituents (e. g. oligooxyethylene groups, carbohydrates, crown ethers) at different lateral positions. Despite of their rigid calamitic structure, some of these compounds form columnar liquid crystalline phases. These columnar mesophases can be stabilized by addition of protic solvents. Binary phase diagrams of selected compounds with water will be discussed. Some crown compounds (e.g. comp. 1) form lyotropic liquid crystalline phases only in the presence of certain cations. This is an interesting example for mesophase formation induced by a molecular recognition processes.

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## D3P.05

SYNTHESIS OF DISCOTIC LIQUID CRYSTALS WITH UNPAIRED SPINS, J. M. Farrar, J. Huang, and P. Kaszynski, Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN, 37235, USA.

Discotic liquid crystals with an unpaired electron delocalized in the rigid core are attractive systems for studying spin-spin interactions, unidimensional conductivity, and photoconductivity in columnar and rigid solid phases. The magnitude of the intermolecular interactions can be controlled by type of mesophase, which, in turn, can be influenced by substituents.

Our molecular design of such a class of discogens is based on dibenzo [c,e][1,2] thiazinyl radical which was shown to be persistent and only slightly sensitive to oxygen [1]. Here we report the synthesis and properties of the first two members of this new family of discotic LC.

[1] P. Kaszynski, M. K. Patel, and J. Huang, Mol. Cryst. Liq. Cryst. 272, 87 (1995).

#### **D3P.06**

THE SYNTHESIS OF DISCOTIC LIQUID CRYSTALS BASED ON THE TRIPHENYLENE NUCLEUS TO FORM ALIGNED MONOLAYERS, Heather Allinson, Neville Boden, Richard J. Bushby, Stephen D. Evans and Philip S. Martin, SOMS Centre, University of Leeds, Leeds, LS2 9JT.

Discotic molecules based on the triphenylene nucleus, incorporating both thioethoxyethoxy- and hexyloxy- side chains have been synthesised for the purpose of creating specifically oriented molecular layers over a gold surface, the main synthetic route to the triphenylene core being the well established ferric chloride oxidative coupling route devised at Leeds University [1]. The Self assembled monolayers (SAMS) are formed by adsorption of the discotic molecule from solvent solution onto a clean gold surface and by varying the number of thiol side chains in the systems considered, different alignments of molecular cores are created with respect to the surface. The influence these SAMS have upon bulk liquid crystalline materials, calamitic or discotic, deposited over these films are considered. The use of optical microscopy and evanescent wave ellipsometry [2] to study the interactions of liquid crystals with these discotic SAMS is discussed. These techniques allow the bulk and interfacial orientation of liquid crystals to be studied.

[1] N. Boden, R. J. Bushby, A. N. Cammidge, G. Headdock, Synthesis, (1995), 31

[2] H. Allinson, N. Boden, S. D. Evans, J. R. Henderson, Phys. Review Lett., 1995, in preparation.

COLUMNAR MESOPHASES BASED ON NON-DISCOID METAL COMPLEXES. S. T. Trzaska, H. Zheng, and T. M. Swager, Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA, 19104-6323

A common approach to columnar liquid crystals is to use planar disc-shaped molecules. We report liquid crystals based on a variety of non-discoid metal  $\beta$ -diketonate complexes. The half-disc square planar rhodium and iridium  $\beta$ -diketonate complexes (I) exhibit  $\Phi_h$  phases by organizing in an antiparallel arrangement. Octahedral cobalt, chromium, manganese, and iron complexes (II) have also been found to display novel  $\Phi_h$  phases. The syntheses, liquid crystalline properties, and possible applications will be discussed.

$$\begin{array}{c} & \text{II} \\ & \text{Ro} \\$$

**D3P.08** 

DISK - LIKE MESOMORPHISM PREDICTION OF PHTHALOCYANINE AND PORPHINE DERIVATIVES, O.B.Akopova, S.A.Zdanovich, A.A.Akopov, N.V.Usol'tseva\*, PLLC, Ivanovo State University, Ivanovo, 153025, Russia.

The method of calculation and analysis of molecular parameters (MP) for preliminary estimation of diskophase appearance for new hypothetic disk-like structures was suggested earlier [1]. Here we analyze data for a new sample of disk-like compounds, that have phthalocyanine or porphine macrocycle as a central fragment. We have calculated MP:  $K = L_{max}/s$ ,  $K_c$ ,  $K_p$ ,  $K_s$ ,  $M_m$ ,  $M_r$ , built histograms and  $K_p$ ,  $M_m$ ,  $M_r$  parameters distribution functions, estimated the probability of mesomorphism appearance by MP for 200 phthalocyanine and porphine structures with well known mesomorphic properties. Then the new series of hypothetic molecular structures with central porphine core was studied. The nature and the length of perepherical substitutes were varied. The structures for which diskophase appearance was the most probable were selected by values of the parameters mentioned above. Five structures were chosen from 66 ones. They will be synthesized for prognosis verification.

[1] Akopova O.B. at all, (Russ.) Phis. Chim. 64. 1460 (1990); 69. 98 (1995); 70. 457 (1996). \*Supported by EC "Molecular Organization in Liquid Crystals".

D3P.09

SYNTHESIS OF CHIRAL TETRAZINE DERIVATES AND THEIR BEHAVIOR IN THE LIQUID CTRYSTAL DISPLAY, Guo Du Ren, X.L. Yuan and J.R. Wang, Department of Fine Chemical Technology, Dalian University of Technology, 158 Zhongshan Rd, Dalian, 116012, China

It was reported that many tetrazine compounds absorb visual light and exihibit negative dichroism<sup>[1,2]</sup>. In this work, two series of symmetrical and unsymmetrical chiral Tetrazines from 3,6-dioxybenzotetrazine have been synthesized. The starting optically active (S)-chlorocarboxylic acids were prepared from correspondingly  $\alpha$ -amino acids. Some of the synthesized compounds above had not been reported. Their structures were identified by IR,MS, H-NMR and elemental analysis. It was found that some of the synthesized chiral tetrazines possess liquid crystalline phases by DSC and polarization microscope. Their order parameters in E63 were also measured.

- [1] D.Demus et al., DD WP,137117(1978)
- [2] Sun Xi Cheng, Ren Guo Du, Organic Chemistry, (8), 365 (1988), China



SYNTHESIS AND PROPERTIES OF CHIRAL LIQUID CRYSTALLINE TEREPHTHALIC ACID DERIVATIVES, K.Fodor-Csorba, G.Galli<sup>\*</sup>, A.Vajda, S.Holly\*, E.Gács-Baitz\*, K.Újszászy<sup>†</sup>, L.Bata, Res. Inst. for Solid State Phys. of Hung. Acad. Sci., H-1525 Budapest, POB. 49., Hungary, Dept. of Chem. and Ind. Chem. Univ. of Pisa, 56126 Pisa, Italy, \* Centr. Res. Inst. for Chem. of Hung. Acad. Sci., H-1525 Budapest POB. 17., Hungary, † EGIS Pharm. Co., H-1475 Budapest, POB. 100., Hungary One, three, and five rings containing polyester derivatives of terephthalic acid were prepared. (S)-2methylbutyl and (R)-2-chloropropyl alcohol were used as chiral starting materials. Three different ester forming procedures were examined. Racemization was observed during the preparation of (R)-2-chloropropyl esters by direct ester formation. No racemization was detected when dicyclohexyl carbodiimid was applied as coupling agent, but the purification of the final product became difficult. Ethoxy-carbonyl-oxy protecting group was choosen to avoid these problems. All the intermediates and final products were examined by IR, NMR and MS. The phase transitions were examined by optical microscopy and DSC. The one ring containing terephthalic ester derivatives did not exhibit any liquid crystalline properties but served as chiral dopants in ferroelectric mixtures. The three ring systems had enantiotropic cholesteric and monotropic smectic A phase. Most of the compounds exhibited blue phase as well. The compounds containing five rings in their core system exhibited cholesteric phase, further on the formerly monotropic smectic A phase has been stabilized by the longer core system. These compounds were applied in ferroelectric mixtures.

## **D3P.11**

NEW LIQUID CRYSTALLINE TIO-SUBSTITUTED PYRIDINES, A.I.Pavluchenko, E.P.Pozhidaev\*, A.L.Andreev, S.I.Kompanets, Organic Intermediates & Dyes Institute, B.Sadovaya 1-4. Moscow, 103787, Russia; \*P.N. Lebedev Physical Institute, Leninsky pr.53, Moscow, 117924, Russia.

The synthesis of 2-(4-tio-alkylphenyl)-5-alkyl-pyridines: 
$$C_nH_{2n+1}$$
 -  $O$  
is discussed. The general method of the synthesis has been described earlier[1]. Some properties, such as mesophase succession and phase transition temperatures versus n and m are investigated. These substances possess isotropic, smectic A, smectic C and smectic F mesophases. Phase diagrams of binary systems containing smectic F tio-substituted pyridines are described. Rotational viscosity  $\gamma_{\phi}$  of smectic C and smectic F versus temperature T was measured also. The  $\gamma_{\phi}$  (T) dependence in smectic F in comparison with the smectic C one is discussed.

[1] A.I.Pavluchenco, N.I.Smirnova, V.F.Petrov, Mol. Cryst. Liq. Cryst., 209,155 (1991).

## D3P.12

OPTICALLY ACTIVE DOPANTS INCORPORATING A 2,4-DISUBSTITUTED OXAZOLINE RING, A. G. M. Lamb, M. Hird, S. M. Kelly and J. W. Goodby, The School of Chemistry, The University of Hull, Hull, HU6 7RX, UK.

A variety of 2,4-disubstituted oxazolines has been prepared easily from readily available nitriles and optically active amino alcohols in a one step, zinc-catalysed reaction. The aromatic core and the terminal chains have been varied systematically and the effect on the liquid crystal transition temperatures evaluated. Although the fully aromatic oxazolines are generally not mesomorphic, those containing at least one 1, 4-disubstituted cyclohexane ring exhibit smectic mesomorphism including smectic A and ordered smectic phases. Chain branching in the alkyl chain at the chiral centre leads to lower transition temperatures. These optically active materials can be used as chiral dopants to generate chiral nematic and smectic C mixtures from achiral precursor mixtures. An unusual phenomenon of some of the chiral smectic C mixtures is the observation of a TGB phase, although the pitch of the chiral dopant is relatively long.

## NOVEL FERROELECTRIC AND ELECROCLINIC ORGANOSILOXANE LIQUID CRYSTALS

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We report the synthesis and physical studies of a new series of organosiloxane ferroelectric liquid crystalline materials. These materials contain a siloxy chain attached to the hydrocarbon chain at the nonchiral end of the molecule. All materials show a very low melting point (<0 °C) and exhibit chiral smectic A (SmA) and chiral smectic C (SmC\*) mesophases. The changes in the siloxy and hydrocarbon chain lengths strongly affect the mesomorphic behavior and electrooptic properties of these materials. The electroclinic effect in the smectic A phase is characterized by a large induced tilt angle (greater than 22.5°) at very low voltages. The effect of the length of the siloxy and hydrocarbon chains on the spontaneous polarization in the SmC\*, switching times, and induced tilt angle in SmA will be presented.

D3P.14

EFFECT OF ABSOLUTE CONFIGURATIONS ON THE FORMATION OF TGB<sub>A</sub> PHASE IN DOUBLE CHIRAL LIQUID CRYSTALLINES, <u>W.J. Hsieh</u> and S.L. Wu, Department of Chemical Engineering, Tatung Institute of Technology, Taipei 10451, Taiwan R.O.C.

We have shown in previous work[1] that a homologous series of double chiral materials (2R)-pentyl (2S)-2-(6-(4-(4'-alkoxyphenyl)benzoyloxy-2-naphthyl)propionates, (R,S)PmPBNP (m=7-14), exhibits  $TGB_A$  phase. Amongst them, (R,S)P10PBNP possesses the most stable  $TGB_A$  phase of approximate 28.2°C temperature range with phase transition sequence:  $I-N^*-TGB_A-S_C^*-K$ . To understand the effect of relative configuration of double chiral tail on the appearance of  $TGB_A$  phase, a diastereomeric compound (S,S)P10PBNP has been synthesized and its mesophases investigated. The result indicates no existence of  $TGB_A$  phase and the sequence becomes:  $I-N^*-S_A-S_C^*-K$ . Furthermore detail study in binary mixture of two diastereomers show that as the (R,S)-form dominates ( $\geq 73\%$ ) in the mixture,  $TGB_A$  phase remains as thermodynamic stable as its pure form. The stability of  $TGB_A$  phase gradually reduces as the contain of (R,S)-form decreases and disappears at the contain of (R,S)-form less than 25%. Our results demonstrate that the absolute configuration of double chiral tail in liquid crystallines could affect to the formation of  $TGB_A$  phase.

[1] S.L. Wu and W.J. Hsieh, in "5th International Conference on Ferroelectic Liquid Crystals", Cambridge UK, 471(1995).

D3P.15

STABLE TGB<sub>A</sub> PHASE IN A SERIES OF CHIRAL MATERIALS DERIVED FROM (R)- AND (S)-3-ETHYLMERCAPTO-2-METHYL PROPIONIC ACID, S.L. Wu and J.H. You, Department of Chemical Engineering, Tatung Institute of Technology, Taipei 10451, Taiwan R.O.C.

A homologous series of chiral liquid crystallines, (R)- and (S)- 6-(3-ethylmercapto-2-methylpropionyloxy)-2-naphthyl 4-alkoxybenzoates, (R)- and (S)-EMMPNmB (m=6-12), has been synthesized for the study. Mesophases were characterized by polarizing microscope, DSC and other electro-optic methods. It was found that compound of m=7 is not mesogenic. A stable microscopic texture of spiral filaments was found as the alkyl chain length m $\geq$ 8. This texture characterized as TGB<sub>A</sub> phase was further confirmed by the formation of focal conic texture of S<sub>A</sub> phase by the racemic mixtures. Ferroelectric S<sub>C</sub>\* phase occurred as m $\geq$ 9. Detail mesophases as function of alkyl chain length and some electro-optic properties of S<sub>C</sub>\* phase such as spontaneous polarization, tilt angle and dielectric constant will be presented and discussed.

FUNCTIONALISATION OF CHIRAL LIQUID CRYSTALS BASED ON 2,6-DIPHENYL-1,3,5-TRIOXA-DECALIN, M. von Minden, Matthias Paul, H.-W. Tunger, and V. Vill,\* Institute of Organic Chemistry, Martin-Luther-King Platz 6, 20146 Hamburg, Germany

Diphenyltrioxadecalins are easily accessible from glucose. These compounds show cholesteric, smectic A, monotropic smectic C\*, blue phases and TGBA phases [1]. Small modifications in the molecular structure cause a significant change in the mesogenic behaviour: The 2-bora-substitution of the oxadecalins enhances the mesophase range. Terminal nitro and cyano groups cause cholesteric phases with sign inversion or reentrant behaviour of cholesteric and TGBA-phases [2,3]. Ring opening of the oxadecalin system results in trisubstituted tetrahydropyran-mesogens with Y-shapes [4]. The synthesis and properties of the new compounds will be discussed.

[1] V. Vill, and H.-W. Tunger, Liebigs Ann. 1055 (1995).

[2] V. Vill, and H.-W. Tunger, J. Chem. Soc., Chem. Commun. 1047 (1995).

[3] V. Vill, H.-W. Tunger, H. Stegemeyer, and K. Diekmann, Tetrahedron Asym. 5, 2443 (1994).

[4] V. Vill, H.-W. Tunger, and M. Paul, J. Mater. Chem. 5, 2283 (1995).

\*Support by Deutsche Forschungsgemeinschaft

## D3P.17

SYNTHESIS OF A NEW FERROELECTRIC LIQUID CRYSTALLINE COMPOUND WITH

ESTER LINKAGE

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A new ferro electric liquid crystalline compound, 4-(2-butyloxy carbonyl)-Phenyl-4-(4-dodecyloxy carbonyl) benzoate, has been synthesized. The DSC and optical microscopy studies reveals that the compound exhibit ferroelectric and smectic phases at lower and higher temperatures respectively. The NMR & IR spectral studies have also been carried out to verify the ester linkage. The viscosity, pitch, tilt angle and spontaneous polarization are also measured.

1)Isa Nishiyama, Masayuki Saito and Atsushi Yoshizawa, Mol.Cryst.Liq.Cryst. 1795 Vol.263, pp. 123-129.

## D3P.18

NOVEL ANTIFERROELECTRIC LIQUID CRYSTALS DERIVED FROM TRIFLUOROMETHYLATED PYRANOSE. K. Itoh, <u>T. Ishizuka</u>, M. Takeda, M. Namekawa, T. Yamazaki\* and T. Kitazume\*, R & D Dept., Kashima Oil CO.,LTD., 4. Towada, Kamisu-machi, Kashima-gun, Ibaraki-ken, 314-02 JAPAN, \*Department of Bioengineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 JAPAN

We synthesized a new series of trifluoromethylated pyranose derivatives having three member aromatic ring systems. The compounds showed different phase transition sequences due to the configuration of the chiral part. Some compounds showed an SmCA\* phase in the wide temperature range. The compounds also exhibited large spontaneous polarization values (over 700 nC/cm<sup>2</sup>) and high tilt angles.

We will discuss the synthesis, as well as the electrical and physical properties of these compounds.

DIFLUOROBIPHENYL DIOXABORINANES FOR FERROELECTRIC LIQUID CRYSTAL DISPLAY APPLICATIONS, <u>Chu Chuan Dong</u>, Peter Styring, Lawrence K M Chan<sup>§</sup> and John W Goodby, School of Chemistry, University of Hull, Hull HU6 7RX, UK, §Thorn EMI - Central Research Laboratories, Dawley Road, Hayes, Middlesex, UB3 1HH, UK.

A new class of heterocyclic compounds, difluorobiphenyl dioxaborinanes, have been synthesised [1]. The materials were prepared for use in ferroelectric liquid crystal (FLC) mixtures. In this paper we will report the details of the synthesis and mesomorphic properties of these materials. Compounds which are laterally fluorinated in the 2,3-positions of the terminal ring show smectic C and nematic phases for the alkyl-alkoxy homologues and smectic A and nematic phases for the dialkyl homologues. Lateral 2,3-difluorination of the middle ring increases the nematic mesophase range and suppresses smectic phases to such an extent that only smectic C phases appear for longer chain length homologues.

[1] L.K.M. Chan, C. Dong, P. Styring and J.W. Goodby, GB Pat. Appl. 9220189/6. International Pat. Appl. PCT/GB93/01929.

D3P.20

CHIRAL SMECTIC  $^*$ C MESOGENS HAVING ESTER AND AMIDE CENTRAL LINKAGES, R.A. Vora and R.C. Tandel, Department of Applied Chemistry, Faculty of Technology and Engineering, M.S. University of Baroda, Post Box No.51, Vadodara - 390 001, India.

Ten members of a chiral homologous series 4 (4'-n-alkoxy benzoyloxy benzoyl) 4"-s-(+) 2-methyl butoxy anilines were synthesized in multiple step systhesis. Series exhibits chiral smectic \*C and cholesteric mesophases. The effect of amide linkage and chirality is discussed in detail. High temperature cholesteric phases exhibit vivid colours.

D3P.21

SYNTHESIS AND PHYSICAL PROPERTIES OF TFMHPNCBC-d<sub>19</sub>, <u>H. Yin</u>, B. Jin, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, M. Kakimoto, Tokyo Institute of Technology, Department of Organic &Polymeric Materials, O-okayama, Meguro-ku, Tokyo 152, Japan

In our previous X-Ray diffraction studies, we noticed that the layer spacing of SmlA\* is unusually larger than those of SmCA\*. The molecules are expected to have a stretched structure to some extent in SmlA\*, although the chiral alkyl chains of this type of antiferroelectric liquid crystals have bent/oblique structures both in SmCA\* and a crystal phase[1]. In order to study the interesting behavior of the SmlA\*, we have synthesized the target compound (R)-4-(1-trifluoromethylheptyloxycarbonyl)phenyl 4'-nonylcarbonyloxy biphenyl-4-carboxylate (TFMHPNCBC)-d<sub>19</sub>, with deuterated achiral alkyl chain, which exhibits stable antiferroelectric SmlA\* with the phase sequence, Iso-SmA-SmCA\*-SmlA\*-Cryst. In this paper, we will report the synthetic routes of the labelled compound as well as some of the physical properties obtained by polarized FT-IR spectroscopy.

[1] K.Hori and K.Endo, Bull. Chem. Soc. Jpn, 66, 46(1993)

NOVEL FEEROELECTRIC LIQUID CRYSTALS CONTAINING THE BENZO-FURAN MESOGENIC CORE, Xin-Hua Chen\*, D. M. Walba\*, Renfan Shao\*, N. A. Clark\*, \*Dept. of Chemistry and Biochemistry, #Dept. of Physics, University of Colorado, Boulder, CO 80309, USA

A series of novel ferroelectric liquid crystals materials were synthesized. They contain a new mesogenic coresubstituted benzofuran, which was obtained by an intramolecular Wittig reaction.<sup>[1]</sup> The general structure of the new materials is shown below.

This four-ring system exhibits broad liquid crystal phase ranges including SC\*. Several FLCs with large spontaneous polarizations were obtained. In this paper the synthesis and detailed investigation of the ferroelectric properties of these new materials will be presented.

[1]. A. Hercouet, M. Le Corre, Tetrahedron, 37 (16), p2867, 1981

#### D3P.23

INFLUENCE OF THE S<sub>C</sub> HOST ON THE SPONTANEOUS POLARIZATION OF FERROELECTRIC LIQUID CRYSTALS INDUCED BY ATROPISOMERIC BIPHENYLS. Kexin Yang, Bryan Campbell, Despina Vizitiu and Robert P. Lemieux, Chemistry Department, Oueen's University, Kingston, Ontario, CANADA, K7L 3N6.

A novel approach to the design of chiral dopants with high  $P_S$  values has been to introduce an atropisomeric biphenyl group with a fixed transverse dipole moment as part of the rigid core of the molecule (K. Yang & R.P. Lemieux *Mol. Cryst. Liq. Cryst.* 1995, 260, 247). Recent work has shown that compounds such as 1 induce a FLC phase in a number of  $S_C$  hosts, although the magnitude of  $P_S$  strongly depends on the structure of the host. In phenyl benzoate and phenyl pyrimidine hosts,  $P_S$  falls below detection limits (< 0.1 nC/cm<sup>2</sup>) at concentrations of up to 5 mol%; in the host NCB76, a 2 mol% mixture gives a  $P_S$  value on the order of 1.5 nC/cm<sup>2</sup>. These and other results obtained with related atropisomeric dopants will be discussed.

(1) 
$$R = O_2N NO_2$$
  $R = O_3N NO_2$  (NCB76)  $C_7H_{15} = O_2N NO_2$ 

## D3P.24

APPROACHES TO SPONTANEOUSLY POLAR MATERIALS: INVESTIGATIONS OF BOWLIC LIQUID CRYSTALS BASED ON CALIX[4] ARENES, B. Xu, D.-K. Fu, and T. M. Swager\*, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

An extensive investigation has been conducted into the mesomorphic behavior of calix[4]arene based bowlic liquid crystals. The calix[4]arene metallomesogens based on tungsten(VI)-oxo azocalix[4]arenes (I) display highly stable columnar liquid crystal phases. Host-guest effects indicate head-to-tail order within column in which the tungsten-oxo groups protrude into the cavities of the neighboring mesogens. We have successfully developed new methodology to produce optically pure chiral bowlic liquid crystals (II). These compounds are predicted to spontaneously organize into polar liquid crystal phases.

I 
$$M=W$$
. Mo

II-(+)

 $R=C_nH_{2n+1}$ 
 $R=C_nH_{2n+1}$ 

NOVEL DOPANTS FOR FERROELECTRIC MIXTURES INCORPORATING CHIRAL DIOXANE OR TETRAHYDROPYRANE RINGS, <u>Richard Buchecker</u>, Jürg Fünfschilling and Guy Marck, ROLIC Ltd., P.O. Box 3255, CH-4002 Basel, Switzerland.

We have synthesized a series of new compounds incorporating chiral rings 1 to 3a/b and investigated their properties as chiral dopants in ferroelectric mixtures. Compounds with two subunits of 1 in their structures generally exhibit broad mesophases and extremely small helical pitches suitable for DHF

$$R = \begin{cases} F_3C \\ O \\ O \end{cases}$$

$$R = \begin{cases} O \\ O \\ O \end{cases}$$

$$R = Alkyl chain$$

mixtures. Trifloromethyl analogues (2) show no liquid crystalline phases. Some derivatives of 3a exhibit an Sc\*-phase and a small spontaneous polarization while the cis-Isomers 3b lead to a relatively high spontaneous polarizations but not to Sc\*-phases. The so far unknown synthesis of 3a/b, the physical properties of the whole series and the performance in ferroelectric mixtures will be discussed in detail.

D3P.26

SUPRAMOLECULAR ASSEMBLIES FROM LIQUID-CRYSTALLINE PHTHALOCYANINES, C.F. van Nostrum, A.J. Schouten, and R.J.M. Nolte, Dept of Organic Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands.

We describe novel mesomorphic phthalocyanines (Pcs) with fascinating self-assembling properties. Two examples will be highlighted. A Pc with eight chiral (S)-3,7-dimethyloctoxy side chains has been prepared, which forms a chiral columnar mesophase [1]. Highly efficient energy migration over a wide temperature range is observed in this material. Stable bilayers on a water surface can be made from this compound, which can be transferred to form well-organized Langmuir-Blodgett (LB) films. A liquid-crystalline Pc containing four crown ether rings has been synthesized. This compound strongly aggregates in organic solutions to form gels in which extremely long individual stacks of molecules are present, as visualized by electron microscopy [2]. In these stacks electron and ion conducting pathways are present, making these superstructures a new type of molecular wire. Monolayers of a derivative of the crowned Pc on a water surface are able to complex K<sup>+</sup> ions in a non-linear way.

[1] C.F. van Nostrum et al., Chem. Eur. J. 1, 171-182 (1995).

[2] C.F. van Nostrum et al., J. Am. Chem. Soc. 117, 9957-9965 (1995).

**D3P.27** 

ROOM TEMPERATURE LATERAL DIFLUORO-TOLANES FOR HIGH CONTRAST DISPLAYS, S. T. Wu, Hughes Research Laboratories, Malibu, CA 90265; C. S. Hsu and J. M. Chen, Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050

We report on the phase transition temperatures and physical properties of some lateral difluoro-tolane liquid crystals. Their structures are shown below:

$$C_nH_{2n+1} \longrightarrow C \equiv C \longrightarrow C_mH_{2m+1}$$

We have synthesized several homologues with m=6 and n=2-7. Some homologues exhibit nematic phase at room temperature and clearing point near  $100^{\circ}$ C. Their heat enthalpy of fusion is very small. Thus, these compounds are very useful for forming eutectic mixtures with wide nematic range. The dielectric anisotropy of these compounds is about -6. This large negative dielectric anisotropy originates from the dipole moment which is perpendicular to the principal molecular axis. [1] The birefringence of these compounds is about 0.16 at  $\lambda=589$  nm. We foresee potential applications of these compounds for high contrast LC displays using homeotropic alignment.

1. I. C. Khoo and S. T. Wu, "Optics and Nonlinear Optics of Liquid Crystals" (World Scientific, Singapore, 1993).

## METALLOMESOGENS: DISPLAYS, CAGES, RINGS AND STRINGS

I. M. Saez, S. Tantrawong and P. Styring, School of Chemistry, The University of Hull, Hull HU6 7RX, UK.

Metallomesogens derived from 1,3-diketonate [1] and Schiff's base ligands, incorporating an oxovanadium(IV) metal centre have been synthesised and their electro-optic properties evaluated. The complexes show rich mesomorphism which can be controlled by subtle modification of the ligands. A prototype optical storage device will be demonstrated which has multi-session 'write-read-erase' capabilities. We will also present details of some exciting new supramolecular metallomesogens which are covalently bonded to form oligomeric and polymeric cages, rings and strings. Each mesogenic, transition metal-containing core is singularly attached to the supramolecular skeleton to give the target macromolecule. The synthesis, mesomorphism and full structural characterisation of the complexes will be presented. In order to verify the proposed structures we have undertaken comprehensive x-ray crystallographic, FAB MS, GPC and osmometry studies. All confirm the materials to be free from cross-linking. These novel materials open up the possibility of novel applications for metallomesogens away from conventional electro-optic displays.

[1] S. Tantrawong, P. Styring and J. W. Goodby, J. Mater. Chem., 1993, 3, 1209.

#### D3P.29

LIQUID CRYSTALLINE ALKYLENE AMIDE DERIVATIVES, <u>G. Lattermann</u>\*a, U. Stebani<sup>a</sup>, A. Facher<sup>a</sup>, R. Festag<sup>b</sup>, M. Wittenberg<sup>b</sup> J. H. Wendorff<sup>b</sup>, M. Neundorf<sup>c</sup>, S. Diele<sup>c</sup>; aMakromolekulare Chemie I, Universität Bayreuth, D-95440 Bayreuth, Germany; Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany; Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany

New results on cyclic, linear and branched, liquid crystalline alkylene amide derivatives are presented. This comprises the homologous series of mesogens with the smallest azacyclic, i.e. the 1,3,5-triazacyclohexane core. Than, different homologous series of low molecular and polymeric linear alkylene amides with different chain length, but also with different length of alkylene bridges and several related mesogenic examples with ester and urea endgroups will be discussed. Finally, dendrimeric analogues will be introduced.

The mesomorphism of these different classes of alkylene amide mesogens can no longer be explained in conventional terms of molecular or supramolecular anisometry.

#### **D3P.30**

## ON THE MESOMORPHIC PROPERTIES OF NEW ARYL ESTERS OF CARBOCYCLIC AND HETEROCYCLIC ACIDS.

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New aryl esters of some carbocyclic and heterocyclic acids have been obtained

$$\begin{array}{c} H_{2n+1}C_{n}\text{-}(\overbrace{K})+\overbrace{K_{2}}\text{-}coo-\overbrace{-} & \begin{array}{c} Y_{1} & Y_{2} \\ K_{3} & -C_{m}H_{2m+1} \\ Y_{3} \end{array}$$

n,m = 3-7,  $K_1 = benzene$ , cyclohexane, [2,2,2] bicyclooctane, 1,3,2-dioxaborinane;  $K_2 = benzene$ , cyclohexane, Cyclohexane, Cyclohexane;  $Y_1 = H$ ,  $CH_3$ ;  $Y_2 = H$ , CI, O,  $CH_3$ ,  $C_2H_5$ ;  $Y_3 = H$ ,  $CH_3$ 

The mesomorphic properties of the esters have been studied. The results are discussed in terms of the structural differences of the compounds and differences of calculated torsion angles, energies and the distributions of the charge density of the molecules.

• π-RADICAL LIQUID CRYSTALS: DESIGN AND SYNTHESIS, <u>P. Kaszynski</u>, J. M. Farrar, J. Huang, and M. K. Patel, Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN, 37235, USA.

Purely organic paramagnetic mesogens are very rare. Most of them contain a nitroxyl radical attached to a flexible tail, but none has a neutral spin delocalized in the rigid core of the molecule. Such materials are being sought for studies of spin-spin interactions in ordered and semi-ordered media. Recently, we have developed a general design for a broad class of calamitic and discotic liquid crystals with a  $\pi$ -delocalized unpaired electron [1].

Here we discuss our design (with emphasis on spin distribution and radical stability), synthetic methodology, and experimental progress toward this new class of compounds.

[1] P. Kaszynski, M. K. Patel, and J. Huang, Mol. Cryst. Liq. Cryst. 272, 87 (1995).

D3P.32

SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALS CONTAINING THE *p*-CARBORANE MOIETY, J. Laska and <u>P. Kaszynski</u>, Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, TN, 37235, USA.

We have demonstrated that compounds containing 10- and 12-vertex p-carboranes show mesogenic properties [1]. Here we present an efficient synthesis of new liquid crystalline materials, such as 1, with emphasis on heterodisubstituted derivatives of p-carborane. Thermal analysis data indicates that these compounds show lower isotropic transitions than the corresponding bicyclo[2.2.2]octane and phenyl derivatives.

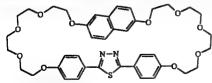
We will also discuss dielectric and photochemical characterization of these new materials.

[1] P. Kaszynski, J. Huang, G. S. Jenkins, K. A. Bairamov, and D. Lipiak, Mol. Cryst. Liq. Cryst. 260, 315 (1995). P. Kaszynski and D. Lipiak, Materials for Optical Limiting, MRS 374, 341 (1995).

D3P.33

LIQUID CRYSTALLINE CYCLOPHANES, B. Neumann, T. Hegmann, D. Joachimi, N. Spencer<sup>+</sup>, C. Tschierske<sup>+</sup>, Department of Organic Chemistry, University Halle, D-06099 Halle, Germany and <sup>+</sup>School of Chemistry, University Birmingham, Edgbaston, Birmingham B15 2TT, UK.

Various cyclophanes incorporating 4,4'-biphenyl, 2,5-diphenyl-1,3,4-thiadiazole-, phenylpyrimidine-, phenyl benzoate and 2,7-disubstituted naphthyl rigid cores were synthesized and their mesomorphic behaviour was studied. Most of these macrocyclic compounds possess liquid cystalline properties with unexpectedly high clearing temperatures compared to those of conventional calamitic mesogens. In this way the coupling of two appropriate rigid units using flexible chains to form a macrocycle constitutes a new and powerful approach towards mesophase induction and stabilization. The type of mesophases formed by these macrocycles does not only depend on the nature of the bridging chains but also depends strongly on the structure of the rigid aromatic



system. The smectic A-phase and the smectic E-phase are formed by biphenylophanes. Cyclophanes incorporating the 2,5-diphenylthiadiazole rigid core form the nematic and the smectic C-phases. A smectic phase is induced by addition of TNF to the nematic naphthaline derivatives. This is the first example of mesophase induction by TNF in the case of calamitic mesogens.

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SYNTHESIS AND MESOMORPHIC PROPERTIES OF LIQUID CRYSTALS MATERIAL CONTAINING FLUOROCARBON / HYDROCARBON TAILS DERIVED FROM 4,4'-BIPHENYL. Frédéric GUITTARD<sup>1</sup>, Elisabeth TAFFIN DE GIVENCHY<sup>1</sup>, Frédéric BRACON<sup>1</sup>, Pierre SIXOU<sup>2</sup> and Aimé CAMBON<sup>1</sup>.(2)Lab. Phys. Mat. Cond. (1)Lab. Chim. Org. Fluor; Université de Nice-Sophia Antipolis, Faculté des Sciences, B.P. N°.71, 06108 Nice Cedex 2, France.

New compounds of the type unsymmetrical disubstituted biphenyls have been synthesized. Two different chains (one hydrocarbon and the other fluorinated) are linked through a connector to a 4,4-biphenyl. Their mesomorphic properties have been characterized by light microscopy and by differential thermal analysis showing the peculiar contribution of the hydrocarbon chain and the fluorinated tail. The enhancement of the hydrocarbon moiety leads to a decrease of the clearing temperatures, furthermore the enantiotropy is changed to the monotropy. The variation of the fluorinated moiety has generated a stabilization of the transition temperatures. The modification of the shape of the connector influences the stability of the mesophase and can, in some cases, completely suppress the liquid crystal character. These mesomorphic properties are compared to their monocatenar perfluorinated analogues incorporating a connector of type ester or primary amide and a series of mixed bitailed previously described [1]. We report in more details their synthesis and their mesomorphic properties.

[1]: F. Guittard, P. SIXOU and A. Cambon, Liquid Crystals, 19, (5), 667, (1995).

## D3P.35

SUPRAMOLECULAR LIQUID CRYSTALS. HYDROGEN-BONDED COMPLEXES BUILT BY SELF-ASSEMBLY OF 2,6-DIAMINOPYRIDINES AND BENZOIC ACIDS, <u>Takashi Kato</u> and Masumi Ogasawara, Institute of Industrial Science, The University of Tokyo, Minato-ku, Tokyo 106, Japan

Supramolecular self-assembly process through molecular interactions such as hydrogen bonds has been shown to be useful to achieve architectures of liquid crystals [1,2]. We report a new family of supramolecular liquid crystals built through the formation of double hydrogen bonds between 2-aminopyridine and benzoic acid moieties. The complexes consisting of 2,6-bis(acylamino)pyridines and 4-substituted benzoic acids show monotropic mesomorphic behavior. For example, the 1:1 complex of 2,6-bis(caproylamino)pyridine and 4-dodecyloxybenzoic acid exhibits a monotropic smectic B phase from 80 to 69 °C. It is interesting that the structure of these molecular complexes is not simple rods or discs. In this complex, the 2,6-bis(acylamino)pyridines unit, which is useful for molecular recognition process, functions as a part of the mesogen. We discuss the structure-properties relationships on these hydrogen-bonded liquid crystals.

[1] T. Kato, in "Handbook of Liquid Crystals", VCH, in press. T. Kato, Supramol. Sci. in press. T. Kato and J. M. J. Fréchet, Macromol. Symp. 98, 311 (1995); J. Am. Chem. Soc. 111, 8533 (1989).

[2] T. Kato, Y. Kubota, M. Nakano, and T. Uryu, Chem. Lett. 1995, 1127. T. Kato, M. Nakano, T. Moteki, T. Uryu, and S. Ujiie, Macromolecules 28, 8875 (1995)

## D3P.36

A CONVENIENT METHOD FOR SYNTHESES OF TRANS-4-(TRANS-4-N-ALKYLCYCLOHEXYL) CYCLO HEXYLCARBONITRILES, Jia Ru Wang, Y.Chen, Z.P.Li, and G.D.Ren, Dept. of Fine Chemical Technology, Dalian University of Technology, 158 Zhongshan Rd, Dalian, 116012, China

Trans-4-(trans-4-n-alkylcyclohexyl)cyclohexylcarbonitriles are important liquid crystal components used in TN and STN-LCD. They're synthesized by using alkylcyclohexanones as main starting material via catalytic hydrogenation of alkylcyclohexylbenzonic acids<sup>11</sup>. In this paper a convenient metod for sytheses of these compounds has been studied. They're synthesized by using cyclohexenc as starting material, in which the hydrogenation of alkylcyclohexylbenzonic acids is by using sodium and alcohol instead of catalytic hydrogenation. The optimum yield of 66% is obtained. The structures of liquid crystals and intermediates are identified by IR,MS, and elemental analysis.

[1] GB 1554131(1978)

SYNTHESIS OF NEW FLUORESCENT MESOGENS 4'-n ALKOXY
BENZOYLOXY 3" CHLORO 4" FLUORO AZO BENZENES N.K.Chudgar'
H.C. Sharma, Department of Chemistry, Faculty of Science, M.S. University of
Baroda, Baroda - 390 002. India.

Recently we have reported on few mesogenic systems with lateral hydroxy substituent ortho to ester linkage and azine linkage (1-2). Studying the lateral substituent, it was of interest to study the effect of halo group terminally and laterally substituted with azo group as one of the central linkage. The present series 4'n alkoxybenzoyloxy 3" - chloro, 4" -fluoroazo benzenes was synthesised. In this homologous series methoxy derivative was nonmesogenic in character, whereas all other members exhibited mesomorphic behavious. Lower members n-ethoxy to n-pentyloxy derivatives exhibit only nematic mesophase. In the n-hexyloxy to n-nonyloxy derivatives exhibited polymesomorphism. Higher members n-decyloxy to n-hexadecyloxy derivatives only a smectic mesophase appears. The resulting homologous series was characterized by elemental analysis and spectroscopic technique. The thermal stability of the present series was compared with that of other series. Fluorescent spectral study are also carried out.[1] N.K.Chudgar, H.C.Sharma, Alpana Shah Mol.Matt, 4 283-287 (1994). [2] N.K.Chudgar, H.C.Sharma, A.M.shah Mol.Matt, (in Press) (1995).

**D3P.38** 

Synthesis of 2 Hydroxy 4-n Alkoxy Benzolc Acids. N.K. Chudgar & H.C. Sharma, Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda - 390 002. India.

Recently we have reported ortho hydroxy derivatives with different moleties. To evaluate the mesogenic properties and it's effect of subsituent on mesomorphic thermal stabilities and indeed the influence of terminal substitutent on alkoxy benzoic acid as well as effect of introducing hydroxy group at 2-position of 4-n alkoxy benzoic acids. This was done in order to understand the effect of substitution which led to increase in molecular breadth. Both smectic and nematic mesophase depend to a greater extent on these cohesive forces and to maintain the orientation of the molecules. The present series of 2 hydroxy 4-n alkoxy benzoic acids was synthesized. The synthesized compounds were characterized by elemental analysis and spectroscopic techniques. The first seven homologes of the present series are non mesogenic and mesomorphism appears from octyl derivatives and persistive tradecyl derivative. Hexadecyl derivative is non mesogenic. The transition temperatures are also confirmed by DSC.

**D3P.39** 

MESOGENIC PROPERTIES AND THE EFFECT OF 1,3,4-TRISUBSTITUENTS ON CENTRAL BENZENE NUCLEUS, R.A.Vora, A.K. Prajapati and J.B. Kevat, Department of Applied Chemistry, Faculty of Tech. & Engg., Post Box No. 51, M.S. University of Baroda, VADODARA - 390 001, INDIA.

Number of mesogenic homologous series are synthesized by fixing a rigid 4-substituted phenyl azo group to resorcinol moiety. Both the hydroxy groups are etherified and esterified by n-aliphatic chains and 4-n-alkoxy benzoyl groups, respectively. All these homologues exhibit low melting smectic C phases. Monoesters, having free lateral hydroxy group, due to strong hydrogen bonding, exhibit high temperature nematic phases. Effect of different substitution on mesomorphic properties is discussed.

NEW LIQUID CRYSTALLINE PYRIDINE DERIVATIVES: 4- (4'-n- ALKUXY BENZYLUXY) BENZYLIDENE 2"-AMINO PYRIDINES, Jayrang S. Dave and Meera Menon, Department of Applied Chemistry, Faculty of Tech. & Engg., M.S. University of Baroda, Post Box No.51, Vadodara-390 001, INDIA.

A new mesogenic homologous series of pyridine derivatives viz: 4- (4'-n-alkoxy benzyloxy) benzylidene 2"-amino pyridines; comprising twelve homologues (R=-CH3...n-C8 H17,-C10H21, -C12H25, -C14H29, -C16H33) has been synthesized and its mesomorphic characteristics are studied. The first two members are non-mesogens; exhibition of nematic phase begins from propoxy derivative and exsists upto heptyloxy derivative. The smectic phase commences from octyloxy homologue and persists upto the last hexadecyloxy homologue. The N-I transition curve initially shows rising tendency as the series is ascended; followed by a slight downward slope towards the last member studied. The homologous series is a low melting series and yields interesting comparison with structurally similar homocyclic series.

## D3P.41

SYNTHESES AND POLARIZED SPECTROSCOPIC STUDIES OF NEAR-IR ABSORBING 2-AMINOTHIOPHENOL METAL COMPLEXES, <u>Jodi L. Wesemann</u> and Gerald R. Van Hecke, Department of Chemistry, Harvey Mudd College, Claremont, CA 91711, USA.

Substituted 2-aminothiophenols have been synthesized from substituted anilines and used as ligands in metal complexes. The square-planar complexes, like related 1,2-dithiolene complexes, absorb strongly in the near-IR. Our studies on the the nickel 5-decyl and 5-tetradecyl derivatives will be reported. Incorporation of the long alkyl chains, though failing to induce liquid crystalline behavior, does increase the solublity of the nickel complexes in mesogenic cyanobiphenyl solvents. Polarized spectroscopy of the liquid crystalline solutions reveals the dichroic nature of the near-IR absorption.

D3P.42

SYNTHESIS OF DEUTERATED MHPOBC-d43 AND MHPOBC-d3 AND BEHAVIOR OF METHYL GROUP NEAR CHIRAL CARBON AS OBSERVED BY POLARIZED FT-IR AND NMR SPECTROSCOPY, B. Jin, H. Yin, S. Yoshida, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, M. Kakimoto, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

To elucidate the ferroelectricity and antiferroelectricity in liquid crystals, understanding the behavior of chiral center is very important. For this purpose, we have synthesized two kinds of 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylates (MHPOBCs); one has a deuterated methyl group of the chiral carbon and the other is its inverted compound, fully deuterated except for the methyl group. The degree of deuteration was not less than 98%. Optical resolution was performed by using an HPLC chiral column (Daicel Chiralpak AD) and attained the enantiomeric excess of about 98 %, which proved an effectiveness of this method for some chiral intermediates synthesis. The methyl group of MHPOBC-d43 have three peaks (2970, 2933, 2869 cm<sup>-1</sup>) in IR spectra. The peak of 2970 cm<sup>-1</sup> is due to the ordinary asymmetric mode and its absorbance vs polarizer rotation angle is in-phase with that of phenyl ring stretching which is considered to be parallel to the molecular long axis both in SmA and electrically unwound SmC\*; the peak of 2869 cm<sup>-1</sup> is due to the ordinary symmetric mode and the 2933 cm<sup>-1</sup> peak is an identified one. MHPOBC-d43 gives rise to the triplet peaks seperated about 15 kHz from one another in wideband <sup>1</sup>H NMR, which is caused by the dipolar interactions among the three equivalent protons. Detailed investigations are in progress.

SYNTHESIS AND MESOMORPHISM OF COMPLEX ETHERS CONTAINING PHENYLCYCLOHEXANE FRAGMENTS <u>V.Bykova</u>, M.Zharova, Liquid Crystals Laboratory, Ivanovo State University, Ivanovo, 153025, Russia.

With the aim to find liquourcrystallic compounds using Nenitrescu method [1] through intermediate trans-4-phenylcyclohexane we obtained a number of complex ethers and Shiff bases containing phenyl-cyclohexane fragments [2]. The purity of the compounds was controlled by the data of elementary analysis, thin-layer chromatography and JR-spectroscopy. Mesomorphic properties were investigated, temperature ranges of mesophase existence and the type of mesophase were determined using the method of polarization microscopy and the differential thermal one. It has been determined how the temperature of phase transitions depended on the nature of isolated molecular fragments of the compounds synthesized. It has been shown that the usage of trans-4-phenylcyclohexane circle leads to an assential growth of thermostability of the nematic stage as well as to a decreased temperature of isotropic transition of the compounds synthesized.

[1] C.Nenitrescu, J.Gavat. Lieb. Ann., 1935. Vol.519. P.260-271.

[2] V.Bykova, M.Zharova, L.Karamysheva. J.Chem. and chem.techn. 1993. Vol.7. P.40.

**D3P.44** 

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME 3,6-DISUBSTITUTED CYCLOHEX-2-ENONES, V.S.Bezborodov(\*), R.Dabrowski(+), G.M.Sasnowski (\*), J.Dziaduszek(+); (\*) Institute of Applied Physics Problems, 220064, Minsk, Belarus; (+) Military University of Technology, 01-489 Warsaw, Poland

The synthesis and mesomorphic properties of several dozen 3,6-disubstituted cyclohex-2-enones 1 and 2,

$$R_{1}-K_{1}-(CH_{2}-CH_{2}) = K_{2}-(CH_{2}-CH_{2}) = K_{3}-X$$
 (1) 
$$R_{1}-K_{1}-(CH_{2}-CH_{2}) = K_{3}-X$$
 (2)

wherein the terminal group X is a hydrogen or an alkyl or an alkoxy redical or a halogen atom; m, l are 0 or 1;  $K_1$ ,  $K_2$ ,  $K_3$  are single bonds or benzene or cyclohexene are described. The compounds were obtained by the condensation of hydrochloride of 4-substituted  $\beta$ -N-dimethylaminoethylarylketones or  $\beta$ -N-dimethylaminoethylvinylarylketones (Mannich's salts) with 2-alkylacetoacetic esters. The influence of the structure of the reactants, catalysts and solvents on the yields is shown.

**D3P.45** 

INFLUENCE OF LINEAR FLUORINATED TAIL ON THE MESOMORPHIC PROPERTIES OF SOME SUBSTITUTED SCHIFFS BASES. Frédéric GUITTARD<sup>1</sup>, Pierre SIXOU<sup>2</sup> and Aimé CAMBON<sup>1</sup>.(2)Lab. Phys. Mat. Cond. (1)Lab. Chim. Org. Fluor; Université de Nice-Sophia Antipolis, Faculté des Sciences, B.P. N°.71, 06108 Nice Cedex 2, France.

The synthesis of a series of partially fluorinated liquid crystals has been reported. We report, for the first time, in this work, on the great effect of the introduction of 2-(F-alkyl)ethyl chains connected to 4 biphenyl through a Schiff's base. Even though their hydrocarbon analogues are not mesomorphic, the overall compounds of the F-alkylated series are thermally stable and have a smectogenic enantiotropy within a wide temperature range. Smectic enhancement through incorporation of fluorine into the tails of a liquid crystalline system appears to be quite general in this series of compounds. The decrease in number of fluoromethylene groups leads to a thermotropic polymorphism notably remarkable for F-butyl or F-hexyl. However, the introduction of the methyl group, branching the spacer, strongly reduces the stability of the mesophase and leads to a monotropic behavior. The chemical and thermal stability of fluoroalkyl groups and their mesophase, respectively, allow us to consider them as new liquid crystal materials and to increase the value of the 2-(F-alkyl)ethyl moieties as noteworthy precursors in this field. The synthesis, the physical properties of these novel fluorinated materials are reported and the effect of fluorination on these properties is discussed. All these points are commented on and illustrated by the study realized from the differential thermal analysis and the light microscopy.

## D3P

#### **D3P.46**

LIQUID CRYSTALLINE CHARACTERISTICS OF AZO-KETONES: 4-n-ALKOXYPHENYLAZO 4'-PROPIOPHENONES, <u>Jayrang S.Dave</u>, Meera Menon, Department of Applied Chemistry, Faculty of Tech. § Engg., Post Box No. 51, M.S. University of Baroda, VADODARA-390 001, INDIA.

The homologous series 4-n-alkoxyphenylazo 4'-propiophenones, comprising twelve homologues has been synthesised and its liquid crystalline characteristics are studied. The first two homologues are non-mesogens; the propyl and butyl derivatives exhibit monotropic nematic and enantiotropic nematic mesophase respectively, whereas the homologues from pentyl onwards upto the hexadecyl exhibit only smectic A phase. The S-1 curve shows rising tendency upto the octyl homologue as the series is ascended and then it shows falling tendency upto the last derivative studied. This series is compared with other structurally related series and its smectogenic characteristics are discussed.

### D3P.47

LIQUID CRYSTALS WITH TERMINAL OXIME GROUP, Renu Mahajan and Himani Nandedkar, Department of Applied Chemistry, Faculty of Technology and Engineering, Post Box No. 51, M.S. University of Baroda, Vadodara-190 001, India.

Two homologous series with terminal oxime groups are synthesized to evaluate the effect of oxime group on mesogenic properties of the system. It is observed that the oxime formation eliminates the smectic mesophases exhibited by the parent homologous series. The nematic phase exhibited by mesogens has higher thermal stability because of intermolecular hydrogen bonding.

## D3P.48

NEW MESOGENS WITH TERMINAL CYCLOHEXYL GROUP, R.A. Vora, Renu Mahajan and Himani Nandekar, Applied Chemistry Department, Faculty of Technology and Engineering, Post Box No.51, M.S. University of Baroda, Vadodara - 390 001, India.

Two homologous series, cyclohexyl 4(4'-n-alkoxy-benzoyloxy) benzoates(I) and cyclohexyl 4(4'-n-alkoxy cinnamoyloxy) benzoates(II) were synthesized to evaluate the effect of mono substituted cyclohexyl ring system on mesomorphic properties. It has been shown that active matrix display (AMLCDs) require liquid crystals with low viscosity. Series(I) exhibits monotropic smectic phase from pentyloxy derivative which persists upto hexadecyloxy derivative. Series(II) behaves like normal nematogenic series. The present series are compared with structurally related mesogenic homologous series.

#### NOVEL LIQUID CRYSTALLINE HYDRAZONE DERIVATIVES: THE EFFECT OF MOLECULAR GEOMETRY OF THE LIGANDS ON THE MESOGENIC PROPERTIES OF

Bis[N{4-phenylalkyloxy(4'-alkyloxybenzylidene)benzoyl hydrazone}]
Copper(II) and Oxovanadium(IV) Complexes

Pariti S.S.J.Sastry, Poluri A.Kumar, D.M.Potukuchi and <u>V.G.K.M.Pisipati</u>, Centre for Liquid Crystal Research and Education, Nagarjuna University, Nagarjunanagar-522 510, India Homologues series of N{4-phenylalkyloxy(4'-alkyloxybenzilidene)benzoyl hydrazone}(L) with the structural formula.

 $RO \leftarrow CH = N - NH - CO \leftarrow N = CH \leftarrow OCO = OR$ 

where R = 4 to 12 and their copper (II) (CuL<sub>2</sub>) and oxovanadium (IV) (OVL<sub>2</sub>) metallomesogens have been synthesised and thermally charecterised. The ligands are found to be highly stable mesogens exhibiting smectic liquid crystalline phases in the temperature ranges of 50 to 110 °C. While the copper (II) and oxovanadium (IV) complexes of relevant ligands show nematic and/or smectic polymorphism with their melting points raised by about 40 and 55 °C respectively.

## SYNTHESIS AND CHARACTERISATION OF N(4-n-alkoxy-2-hydroxy benzylidene) 4'-n-alkyl anilines, nO(OH).m

M.Srinivasulu, D.M.Potukuchi, <u>V.G.K.M.Pisipati</u> and D.Saran\*, Centre for Liquid Crystal Research and Education, Nagarjuna University, Nagarjunanagar-522 510, India; \*Department of Physics, Indian Institute of Technology, Kanpur, India.

The synthesis, followed by thermal microscopy and calorimetric investigations are reported on a number of schiff base liquid crystalline 4-n-alkoxy-2-hydroxy benzylidene alkyl anilines, abbreviated as nO(OH).m for n=4, 5 and 9 and m=4 to 14. The effect of hydroxyl group at ortho- position of the aldehyde (that bridges the essential central rigid core) on the thermal range and the occurrence of transition temperatures for the observed nematic and smectic phases are discussed in the light of the available data on other schiff based liquid crystalline compounds. The effect of transverse dipole moment extended by the hydroxyl group is found to be more effective to enhance the biaxial smectic stability in the trans-like configurations of compounds possessing alkoxy end chain with odd number of methylene units.

D3P.51

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME PYRIMIDINYL DIACETYLENES,\* C.M. Hudson, R.A. Shenoy and M.E. Neubert, Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA and R.G. Petschek, Case Western Reserve University, Department of Physics, Cleveland, Ohio, 44106-7079 USA

Several diacetylenes of the type

$$X - \bigcirc - C \equiv C - C \equiv C - \bigcirc - Y$$

were synthesized as potential high optical birefringence nematogens. Mesomorphic properties were determined by hot stage microscopy. A nematic phase was observed when A=C, B=N, Y=CN and  $X=C_6H_{13}$ , but when A=N, B=C, X=CN and  $Y=C_7H_{15}$ , the compound was too unstable to observe any mesophases.

<sup>\*</sup>This material is based on work funded in part by the National Science Foundation Science and Technology Center on ALCOM Grant DMR89-20147.



SYNTHESES AND MESOMORPHIC PROPERTIES OF NEW LATERALLY ATTACHED LIQUID CRYSTALLINE DIMERS. <u>V.Surendranath</u> and D.L.Johnson, Kent State University, Kent, OH, 44242, USA

The molecular structure of dimers, trimers and tetramers are intermediates between low molecular mass and polymeric mesogens. In most cases the mesogenic units are attached *via* their terminal chains while in some cases the mesogenic units are attached laterally. The investigation of the properties of laterally and terminally attached dimers and oligomers help to understand the properties of the polymers better. Very few laterally attached mesogenic dimers<sup>1</sup> are reported in literature as compared to that of terminally attached mesogenic dimers<sup>2-3</sup>. We report here the syntheses and mesomorphic properties of new laterally attached dimers incorporating fluorine moiety.

1. A. Yoshizawa and Nishiyama, Mol.Cryst. & Liq.Cryst., 260,403,1995

2. P.J.Barnes, A.G.Douglass, S.K.Heeks and G.R.Luckhurst, Liq. Cryst., 13, 603,1993.

2. R.W.Date, C.T.Imrie, G.R.Luckhurst and J.M.Seddon, Liq.Cryst., 12, 203,1992.

### D3P.53

SYNTHESIS OF MESOGENIC HOMOLOGOUS SERIES 4-(4'-n-ALKOXYCINNAMOYLOXY)-n-BUTOXYBENZENES AND ITS CALORIMETRIC STUDY.

R.A.Vora and P.R.Vyas Central Laboratory, I.P.C.L., P.O. Petrochemicals, Dist.Baroda.INDIA, 391346

Twelve homologues of series 4-(4'-n-alkoxycinnamoyloxy)-n-butoxybenzenes 4-n-4-n-alkoxycinnamoyl chlorides with reacting synthesized by butoxyphenol.All the homologues of this series exhibit mesomorphism.Pure nematogens of this series exihibit a threaded texture, however, in the polymesomorphic region the series exhibits homeotropic texture. Polymesomorphism of homologues. n-Dodecyloxy smectic mesophase is observed in higher n-hexadecyloxy derivatives exihibit monotropic smectic E phase over and above smectic A phase.DSC study confirms the results of the polarising microscope and also reveals solid-solid transitions. Entropies and enthalpies are calculated which exihibit normal trend in homologous series.

D3P.54

SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME ALKYNYL SUBSTITUTED PHENYL-BENZOATES AND THIOBENZOATES,\*
J.M. Whyde, M.E. Walsh, S.S. Keast and M.E. Neubert, Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA

A number of alkynyl substituted esters of the type

with Z=O or S. Y=R, OR, COR or OCOR were synthesized to determine the effect of a triple bond in the terminal chain on mesomorphic properties. Nematic phases were preferred in both series except when Z=O and Y=COR. These esters showed smectic A phases.

<sup>\*</sup>This material is based on work funded in part by the National Science Foundation Science and Technology Center on ALCOM Grant DMR89-20147.

## NOVEL LIGANDS FOR TRANSITION METAL-CONTAINING LIQUID CRYSTALS. Joe Workman, Department of Chemistry, Centre College, Danville, Kentucky 40422

As part of our search for transition metal-containing liquid crystals, we have developed a library of ligand components. With the library we have been able to mix and match ligand components to synthesize a wide variety of ligands. These ligands have flat aromatic portions, long-chain alkyl portions, and  $N_2O_2$  tetradentate coordination sites. Most of our ligands have benzene as the flat portion of the ligand, but we are in the process of synthesizing triphenylene-based ligands. The coordination sites tend to be of the Schiff-base and polyanionic chelating type. Three of the ligand classes are shown below. Coordination of the ligands to first row transition metals is in progress and characterization of liquid crystalline behavior will follow.

**D3P.56** 

THE INFLUENCE OF STRUCTURE OF MONOARMED CROWN ETHER LIQUID CRYSTALS ON THE MESOMORPHIC PROPERTIES. Qing JIANG. Long-Zhang LI. Ji-Wu RUAN. Cheng FANG and Ming-Gui XIE\*. department of Chemistry. Sichuan University. Chengdu 610064. P. R. China Liang-Yu WANG. Department of Chemistry. Qinghua University. Beijing 100084. China.

Four monoarmed crown ether containing benzo-15-crown-5 unit had been designed and synthesized. It was found that the different bridging group of the crown ethers slightly influenced the melting point of the crown ether liquid crysstals. but strongly influenced the thermal stability of the mesomorphic state. The sequence of increase in the clearing point according to the bridging group order was -NHCO-. -O-CO-. -N = N-. -N = CH-. The dependence of the structrue of the crown ethers on the mesomorphic properties was discussed.

\* project supported by National Natural Science Fondation of China.

D3P.57

MODIFIED SYNTHESIS FOR THE PREPARATION OF ONE RACEMIC ISOMER OF THE MACROCYCLIC TRIMER TPB-(c) 9(3),\* S.S. Keast and M.E. Neubert, Liquid Crystal Institute, Kent State University, Kent, OH, 44242, and R.G. Petschek, Department of Physics, Case Western Reserve University, Cleveland, OH, 44106-7079, USA

properties of a thermotropic biaxial nematic phase. We have modified the original synthesis 2 to obtain only one racemic isomer of this compound using a variety of protecting groups and the different reactivities of the biphenol and phenol to avoid forming multiple isomers. This synthesis is also designed to produce large amounts of materials for physical studies.

[1] J.F. Li, V. Percec and C. Rosenblatt, Phys Rev 48E R1 (1993); J.F. Li, V. Percec, C. Rosenblatt and O.D. Lavrentovich, Europhys. Lett. 25 199 (1994).

[2] V. Percec, M. Kawasumi, D.L. Rinaldi and V.E. Litman Macromolecules 25, 3851 (1992).

\*This material is based on work funded in part by the National Science Foundation Science and Technology Center on ALCOM Grant DMR89-20147.

LIQUID CRYSTALLINE MODEL COMPOUNDS BASED ON 2,5-Bis(4-ALKOXY PHENYLENE VINYLENE)THIOPHENES AS ELECTROLUMINACENT MATERIALS, Minggian He and L.-C. Chien\*, Liquid Crystal Institute, Chemical Physics and NSF ALCOM Center, Kent State University, Kent, OH 44242.

Bis-(phenylene vinylene)]thiophene (BPTs), was investigated as the central core unit in mesogenic molecules 1.

Of particular interest was whether the BPT unit could be self-constrained into a trans-conformation, and thus organize into a liquid crystalline phase. A homologues series of BPTs have been synthesized and found to exhibit the nematic mesophase. The physical properties and light emitting characteristics will be reported. This research was supported in part by the NSF ALCOM Center Grant DMR89-20147.

## D3P.59

NEW SYNTHESIS OF THE LIQUID CRYSTALLINE BICYCLOHEXYLBENZENE DERIVATIVES, G.Sasnovski, V.Bezborodov, Institute of Applied Physics Problems, 220064, Minsk, Belarus; R.Dąbrowski, J.Dziaduszek, Military University of Technology, 01-489 Warsaw, Poland

We propose a new approach to prepare the liquid crystalline bicyclohexylbenzene derivatives. The key stage is the synthesis of 3-(trans-4-arylcyclohexyl)-6-alkyl (or aryl) cyclohex-2-en-1-ones (I) via the condensation of the corresponding Mannich salts with 2-substituted acetoacetic esters (or benzyl methyl ketones) in the presence of a base. We have studied this condensation in various conditions to find the optimum (yields 65-70 %). The catalytic hydrogenation of cyclohexanones (I) in base media (in the presence of potassium hydroxide) gives mainly saturated trans-cyclohexanones which are very promising semi-products for the preparation of different kinds of the LC compounds containing bicyclohexyl fragment. We have carried out the numerous chemical transformations of these ketones: reduction in various conditions, acylation etc. As a result the wide range of LC compounds both known [1] and new ones have been prepared. The phase transition temperatures of these compounds are given.

[1] S.Sugimori et al. (Chisso), EP 62470 (1982); DE 3 223 637 (1982)

#### D3P.60

MESOPHASES INDUCED BY HYDROGEN BOND BETWEEN OLIGOETHYLENE GLYCOL SUBSTITUTED BENZOIC ACID AND STILBAZOLE, C.C. Chang and L.J. Yu\*, Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137, Republic of China

Various oligoethylene glycols were used to replace the alkyl chain of p-alkoxybenzoic acid and 4-alkyloxy-4'-stilbazole. The compounds obtained were nonmesogenic or monotropic. Mesophases were observed via the formation of hydrogen bond between these proton donors and acceptors, but with narrower mesophase temperature ranges as compared to those of parent mixtures. These effects were attributed to the curving conformation of the ethylene glycol unit as suggested from the results of model calculation.

MESOGENIC BEHAVIORS OF 4-CARBOXY- AND 4-PROPENOXY-BENZO-15-CROWN-5 STILBAZOLYL ESTERS, J.J. Tsaih and L.J. Yu, Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137, Republic of China

Mesogens without terminal chain were obtained by connecting benzo-15-crown-5 and stilbazole with carboxy and propenoic acids. A nematic phase was observed for the later on cooling from 145 to 129°C. Hydrogen bond induced nematic and smectic phases with wide temperature ranges were observed for mixtures containing paraand meta-alkyloxy-benzoic acids as proton donors.

**D3P.62** 

AMPHOTROPIC CHARACTER OF ALKALI METAL SALTS OF DIHEXADECYLPHOSPHATE, D. Kardassi, D. Tsiourvas and <u>C. M. Paleos</u>, Institute of Physical Chemistry, NCSR Demokritos, 15310 Aghia Paraskevi, Attikis, Greece

It is well established that dihexadecyl phosphate (DHP) and some of its salts form vesicles in dispersion [1]. In the present study the role of of alkali metal cations on the amphotropic character the salts was investigated as compared to the behaviour of DHP. It has been found that the acid as well as its salts aggregate and organize in water forming stable vesicles. The aggregates originating from the DHP have smaller sizes than the ones derived from the salts as determined with optical and AFM microscopy. The same salts, in contrast to the respective acid, which is not a liquid crystal, exhibit thermotropic smectic liquid crystalline phases being in general stable over wide temperature ranges. The solid-mesomorphic transition of the salts is observed at appoximately 80 °C, while mesomorhic-isotropic transition of the salts ranged from about 210 to 300 °C.

1. (a) A. M. Carmona-Ribeiro, Chem. Soc. Reviews, 209 (1992). (b). M. J. Blandamer, B. Briggs, P. M. Cullis amd Jan B. F. N. Engberts, Chem. Soc. Reviews, 251 (1995).

**D3P.64** 

PHOTOCHEMICAL AND THERMAL E,Z-ISOMERIZATION OF p-MENTHANE-3-ONE 2-ARYLIDENE DERIVATIVES, CHIRAL COMPONENTS OF LC SYSTEMS, L.Chepeleva, T.Drushlyak, L.Kutulya, V.Vashchenko, Sergey Yarmolenko, Institute for Single Crystals, Academy of Sciences of Ukraine, Kharkov 310001, Ukraine

The molecular structure influence on photochemical and thermal E,Z-isomerization of enone fragment have been investigated for the series of 1R, 4R and 1R, 4S diastereomeric 2-(4-X-benzylidene)-p-menthane-3-ones (X=C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>-p-OMe, OMe, Cl, NO<sub>2</sub>, NMe<sub>2</sub>) by the methods UV, IR and NMR <sup>1</sup>H spectro-

 $C_6H_4$ -p-OMe, OMe, Cl, NO<sub>2</sub>, NMe<sub>2</sub>) by the methods UV, IR and NMR <sup>1</sup>H spectroscopy and liquid chromatography. E-isomers efficiently transformed into correspondent Z-isomers being irradiated in isotropic solvents as well as LC systems. The quantum yields of forward (0.3-0.4) and backward (0.07-0.1) photoreactions do not depend on the substituent nature, the excitation wavelength and the solvent polarity, but essentially depend on temperature. It was found that Z-forms possess lower twisting power than E-isomers. Twisting power does not depend on  $C^4$  configuration.

twisting power than E-isomers. Twisting power does not depend on C<sup>4</sup> configuration. Photoisomerization has the triplet mechanism and does not lead to C<sup>4</sup> chiral center inversion. The position of photo steady-state equilibrium depends on the excitation methods (direct or sensitized). This can be used for reversible changes of optical characteristics induced cholesteric LC. Investigated compounds have close total energies of E-and Z-isomers (AM1 calculations and molecular mechanics data). Presumably this is the reason for the thermally activated reversible E z isomerization accompanied by C<sup>4</sup> inversion. However, these thermal processes do not influence on optical properties of LC systems which include investigated chiral dopants.



THE SYNTHESIS OF MAGNETIC AND ELECTRIC ORDERED SYSTEMS ON THE BASE OF THE IRON (III) MESOGENS. Yu.Galyametdinov, G.Ivanova, N.Domracheva, L.Tinchurina, L.Kambulova and I.Ovchinnikov.Kazan Physico-Technical Institute, Russian Academy of Science. Sybirski Tract 10/7, 420029, Kazan, Russia. e-mail: Galyametdinov@sci.kcn.ru

The dielectric and EPR studies of the first Fe(III) mesogenic complex exhibit that it is a low dimensial magnetic system<sup>1</sup> with local ordering of dipole moments<sup>2</sup>. New mesomorphic metal complexes of Fe(III) have been synthesised by interaction mesogenic and non-mesogenic Shiff's bases with FeCl<sub>3</sub> and FeBr<sub>3</sub>. Complexes have been studied by differential scanning calorimetry, NMR in solutions, EPR and far IR (solutions and solid state). The materials display Sa phase. Compound with non-mesogenic ligand exhibit low (for metallomesogens) phase transitions temperatures: C 49 Sa 73 i (°C). Changing Cl on Br ion result in decreasing transition temperatures. Well resolved NMR <sup>13</sup>C and <sup>1</sup>H spectra for paramagnetic iron complexes have been obtained in solutions CDCl<sub>3</sub>. Correlation magnetic parameter (g-factors and integrated intensities of the lines) with molecular structure will be discussed.

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R.Manapov, A. Prosvirin, I. Ovchinnikov. Phys. SolidState, 1994, V.36. No.8 .P. 1174-1177. [2] N. Domracheva, Yu. Galyametdinov, I. Ovchinnikov, Y. Zuev, Ferroelectrics. 1996. in press.

CAPILLARY LOCKING OF POINT DEFECT IN NEMATICS, G.Guidone Peroli and E.G. Virga, 1) Dipartimento di Matematica, Università di Pisa, 56127 Pisa, Italy; 2) Dipartimento di Matematica, Università di Napoli, 60125 Naples, Italy.

It has long been known that the equilibrium configuration with minimum energy of a nematic liquid crystal within a cylinder subject to homeotropic conditions on the lateral boundary is escaped along the axis and possesses no singularity of the orientation field. Then the problems arise of explaining the presence of point defects in capillary tubes and exploring their stability. There is enough evidence to hold that the menisci play a central role in preventing the orientation field around a point defect from unwinding towards the escaped configuration. In this paper we propose a variational model which describes how a point defect interacts with a meniscous. This interaction fades away at a finite distance. When active, it is two-sided: repulsive at first sight and then attractive when the defect comes closer to the centre of curvature of the meniscous. Thus, when a defect is enclosed between two menisci, they can become antagonists, so that there is a metastable equilibrium position where the defect could be *locked* in.

D4P.02

STUDIES OF DEFECTS IN CHIRAL NEMATIC DROPLETS, F. Xu and P.P. Crooker, Department of Physics and Astronomy, 2505 Correa Road, University of Hawaii, Honolulu, HI 96822, USA.

We have studied the textures of chiral nematic droplets as a function of chirality alone using polarized microscopy. At low chirality (pitch P > droplet diameter D), the bipolar or twisted bipolar structure is observed; at high chirality (P < D), the droplet adopts the Frank-Pryce structure. In the Frank-Pryce structure, the radial  $\chi$ -disclination is observed to be escaped, so that the defect structure consists of a boojum of surface charge +2 and volume charge +2, and a central point defect of volume charge -1 [1]. In order to change to the bipolar structure, the surface defect splits into two boojums, each of surface charge +1 and volume charge +1. The central defect then combines with one of the boojums, creating a boojum of surface charge +1 and volume charge 0, which then migrates to the opposite pole, thus creating the bipolar structure. These results will be compared with the previous results of Kurik and Lavrentovich [2].

- [1] G.E. Volovik and O.D. Lavrentovich, Sov. Phys. JETP 58, 1159 (1983).
- [2] M.V. Kurik and O.D. Lavrentovich, JETP Lett. 35, 444 (1982).

**D4P.03** 

THE DIELECTRIC PROPERTIES OF NEMATIC LIQUID CRYSTAL 5CB CONFINED TO TREATED AND UNTREATED ANOPORE MEMBRANES, <u>S.A.Różański</u>, Maria Skłodowska-Curie High School, W.Pola 11, 64-920 Piła, Poland

Broadband dielectric spectroscopy (up to  $10^9$  Hz) is employed to study the molecular dynamics of the liquid crystal 4-n-pentyl-4'-cyanobiphenyl (5CB) in the bulk phase and confined in cylindrical channels of Anopore membranes. It has been shown that the confinement of nematic liquid crystal (NLC) to inorganic filters with regular pores provides a convenient tool for the orientation of the sample in dielectric experiments. In bulk 5CB, with the boundary conditions imposed by our experimental set-up, two relaxation processes are observed. In the Anopore membranes, a separation of the two processes is possible. The frequencies of both processes are found to be unchanged with respect to the bulk phase. We extract the frequency dependence of the dielectric anisotropy  $\delta \varepsilon$  from dispersion curve of  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$ . Two changes of sign of  $\delta \varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp})$  are detected as predicted in the literature. The dielectric measurements in untreated Anopore membranes confirm the planar axial order of nematic molecules; in membranes treated by decanoic acid, a polar-radial or polar-polar orientation of the molecules is very likely, although a slight escaped director structure at least at low temperatures seems to be indicated in the dielectric data.



INFLUENCE OF CONFINEMENT ON DYNAMICS OF MOLECULAR MOTION AND COLLECTIVE MODES OF LIQUID CRYSTALS DISPERSED IN PORES, F.M. Aliev, V.V. Nadtotchi, and G. P. Sinha, Department of Physics and Materials Research Center, UPR, San Juan, PR 00931, USA.

We used photon correlation and dielectric spectroscopies to study the influence of confinement on dynamics (molecular motion and collective modes) of nematic liquid crystals (LC) dispersed in porous matrices having different pore structure. We used matrices with parallel cylindrical pores and matrices with randomly oriented, interconnected pores. The average pore size ranged from 100 A up to 2000 A (pore volume fraction 3%-50%). Both methods show modification of dynamics of molecular rotation, director and order parameter fluctuations typical for bulk LC. Moreover qualitative changes in the properties of LC in pores - the appearance of new relaxational processes, supercooling and glass-like behavior, were observed in both matrices with some differences probably due to the fact that the specific area of the interface in matrices with random structure is greater than that in cylindrical pores. A slow mode (typical time > 1ms) was observed in both matrices. The amplitude of this mode increases with decreasing pore size. This fact suggests that this slow process is due to the formation of interfacial layers on the pore walls rather than due to the dynamics of domains. This work was supported by US Air Force grant F49620-95-0520 and NSF grant OSR-9452893.

### D4P.05

COLLECTIVE DYNAMICS OF FERROELECTRIC FREE-STANDING FILMS WITH HIGH SPONTANEOUS POLARIZATION, S.A. PIKIN\*, E.L DEMIKHOV+ and E.S. PIKINA#, \*Inst. of Crystallography, Russian Acad. of Sciences, 117333 Moscow, Russia; + Inst. of Phys. Chem., Univ. of Paderborn, 33095 Paderborn, Germany; # Inst. of Oil and Gas, Leninski pr. 63, 117917 Moscow, Russia Collective dynamics of the SmC\* with high spontaneous polarization has been studied in free-standing films for the first time [1]. A.c. electric field was applied parallel to the smectic layers and the light reflectivity of the films in crossed polarizers was measured. An anomalous reflectivity of resonance type as a function of the a.c. field frequency was observed. The resonance is supressed in high electric fields, at low temperatures in the SmC\* phase and in films thinner that a threshold value N<sub>0</sub>. The obeserved resonance can not be explained as light scattering on the common ferroelectric diffusive modes (Goldstone, soft mode). Concept of kink switching is proposed which consistently describes the observed anomalies. This model assumes that, at the application of electric field E, small areas of the film are reoriented in the first stage and then such a sharply inhomogeneous perturbation is running through the initially homogeneous film. Thus, it is assumed that the boundaries of ferroelectric film produce the certain anisotropic conditions for the distribution of polarization which correlates with assumption made earlier that the structure of thin ferrolectric films of high spontaneous polarization corresponds to the weak anisotropic state. Film parameters: viscosity, dielectric anisotropy and polar film anisotropy are determined. [1]. E.L. Demikhov, S.A. Pikin and E.S. Pikina, Phys. Rev.E 52, 6250 (1995); Journ de. Phys II, 6(5), (1996)

### **D4P.06**

DYNAMICS OF ANNIHILATION PROCESS OF DISCLINATION PAIRS IN NEMATIC LIQUID CRYSTALS, K. Minoura, Y. Kimura, K. Ito, and R. Hayakawa, Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

We have investigated the dynamics of annihilation process of defect pairs in the nematic phase, generated by the annealing process in the isotropic phase. The defects are type-1 wedge disclinations observed as a Schlieren texture with four dark brushes under polarized microscope. The nematic liquid crystal(5CB) sample was sandwiched between two glass plates with one side of homeotropic alignment and the other of free one. We measured the time dependence of the distance d between a defect pair with or without external electric field. The distance d decreased linearly with time immediately after the defect pair was generated (the earlier stage) and then decreased to zero in proportion to the square root of the time to elapse before the defect pair was annihilated (the later stage). We also analyzed the annihilation dynamics by numerical simulation with a 2-dimensional phenomenological equation of motion, and the results were in good agreement with the experimental ones. The ratio of coefficients of viscosity and elasticity, and the strength of ordering field were evaluated from the comparison between the numerical simulation and experimental results.

[1] A. N. Pargellis, P. Finn, J. W. Goodby, P. Panizza, B. Yurke, and P. E. Cladis, Phys. Rev. A46, 7765(1992).

GROWTH DYNAMICS OF ECKHAUS MODES IN ONE DIMENSIONAL ELECTROCONVECTION OF NEMATICS, Y. Hidaka, K. Hayashi and S. Kai, Department of Applied Science, Kyushu University, Fukuoka, 812-81, Japan

The quantative experimental study was achieved for the Eckhaus instability in the electrohydrodynamic instability (EHDI) in one dimensional system in nematic liquid crystals as well as one dimensional Busse baloon. Actually observed Eckhaus wavenumbers and their growth rates agreed well with those of the most unstable modes theoretically expected from the result of the one dimensional amplitude equation.

**D4P.08** 

MONTE CARLO SIMULATIONS OF DEFECTS IN HYBRID NEMATIC FILMS, E. Berggren<sup>1</sup>, C. Chiccoli<sup>2</sup>, O.D. Lavrentovich<sup>3</sup>, P. Pasini<sup>2</sup>, C. Zannoni<sup>1</sup>, <sup>1</sup>Dipartimento di Chimica Fisica ed Inorganica dell'Università, 40136 Bologna, Italy - <sup>2</sup> INFN, Sezione di Bologna, 40126 Bologna, Italy - <sup>3</sup>Liquid Crystal Institute. Kent State University, Kent, Ohio 44242, USA.

We present a Monte Carlo simulation, starting from purely microscopic molecular interactions, of a model nematic liquid crystal film with open boundaries placed between two different media that set antagonistic (planar and homeotropic) polar orientations of the "molecules" at the top and the bottom surface of the system [1]. The molecules, assumed to be three dimensional "spins", lie on the sites of a cubic lattice and interact through the second rank Lebwohl-Lasher potential [2]. To examine the simulated director field we calculate textures under crossed polarizers starting from the Monte Carlo microscopic configurations and using a matrix approach as employed in studying PDLC droplets [3]. It is found that the ground state of the system contains stable topological defects when the lateral radius of the system is larger than its thickness.

- [1] O.D. Lavrentovich and Yu. A. Nastishin, Europhys. Lett. 12 135 (1990).
- [2] P.A. Lebwohl and G. Lasher, Phys. Rev. A 6, 426 (1972).
- [3] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini, and F. Semeria, Phys. Rev. E 50 2929 (1994).

**D4P.09** 

METASTABLE NEMATIC HEDGEHOGS, R. Rosso<sup>1)</sup> and E. G. Virga<sup>2)</sup>, 1)Dipartimento di Matematica, Università di Milano, 20133 Milano, Italy; 2)Dipartimento di Matematica, Università di Napoli, 80125 Naples, Italy.

For nematic liquid crystals, we study the local stability of a radial hedgehog against biaxial perturbations. Our analysis employs Landau-de Gennes' functional to describe the free energy stored in a ball, whose radius is a parameter of the model. We find out that a radial hedgehog may be either unstable or metastable, depending on the values of the elastic constants. For unstable hedgehogs, we give an explicit expression for the radius of the ball within which the instability manifests itself. This radius can be interpreted as the size of the biaxial core of the defect. It possesses the same order of magnitude as the radius of the disclination ring predicted by Penzenstadler and Trebin's model [1], though here two different unstable modes are possible, only one of which shares the symmetry of a disclination ring. The metastable hedgehogs predicted by our model are the major novelty of the paper. They tell us that we may expect also uniaxial point defects, whose core contains no biaxial structure.

[1] E. Penzenstadler and H.-R. Trebin, J. Phys. France 50 (1989), 1027.



THE INFLUENCE OF THE SURFACE-PRETILT ON THE CHEVRON STRUCTURE, S.Kralj<sup>1</sup>, S.Žumer<sup>2</sup> and J.Pirš<sup>3</sup>, <sup>1</sup>Faculty of Education, University of Maribor, Koroška 160, 2000 Maribor, Slovenia, <sup>2</sup>Department of Physics, University of Ljubljana, Jadranska 19, Ljubljana, 1000, Slovenia, <sup>3</sup>Institute Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia.

The influence of the surface-pretilt on the chevron structure of a SmA and SmC liquid crystal confined to a planparallel cell was studied theoretically. The chevron structure was obtained via minimization of the Landau-de Gennes type free energy expressed in terms of the nematic director field and the smectic density wave. We show that the surface-pretilt can not initiate by itself the chevron structure. It can be formed only due to the mismatch between the periodicity enforced by the liquid crystal molecules frozen at the surface and the periodicity of the enclosed smectic phase. The surface pretilt however strongly influences the direction in which the chevron kink is oriented. For large enough surface-pretilt the chevron kink can be oriented only in the direction which the pretilt enforces. We study the chevron evolution as function of temperature for different surface-pretilts. In certain regimes results suggest strong hysteresis phenomena. The influence of the surface-pretilt on the zig-zag defect is also analyzed. Experiment was performed to test theoretical predictions.

### **D4P.11**

VAN DER WAALS-INDUCED DISTORTIONS IN NEMATIC LIQUID CRYSTALS CLOSE TO A SURFACE, P. Galatola, M. Rajteri, C. Oldano, G. Barbero, and S. Faetti\*, Dipartimento di Fisica, Politecnico di Torino, I-10129 Torino, Italy; \*Dipartimento di Fisica, Università di Pisa I-56126 Pisa, Italy.

By a discrete-layer model, we theoretically investigate the alignment of a nematic liquid crystal close to a flat amorphous substrate. We show that the presence of van der Waals interactions, depending on the orientation of the molecules with respect to their relative position, induces a strong distortion localized in a few molecular lengths. These results are compared with those obtained in the framework of a continuum model, in which the molecular density, as well as the nematic order parameter, is supposed to be uniform. In the continuum model, we derive approximate analytical expressions for the distortion profile, showing that asymptotically the distortion decays as the inverse of the distance from the substrate. The amplitude of the distortion according to the two models is different, but the main qualitative features remain unchanged. We show that the main distorting mechanism can be attributed to an effective surface field. The existence of a subsurface distortion is compatible with some recent measurements of the alignment of the first molecular layer, performed with optical second-harmonic generation techniques [1].

[1] Xiaowei Zhuang, L. Marrucci, and Y. R. Shen, Phys. Rev. Lett. 73, 1513 (1994).

### D4P.12

ANNIHILATION OF POINT DEFECTS IN NEMATICS, G. Guidone Peroli<sup>1)</sup> and E. G. Virga<sup>2)</sup>, 1)Dipartimento di Matematica, Università di Pisa, 56127 Pisa, Italy; 2)Dipartimento di Matematica, Università di Napoli, 80125 Naples, Italy.

Point defects are likely to be generated in the process of filling a capillary tube subject to homeotropic conditions on the boundary. There is plenty of experimental evidence to hold that, when two defects with opposite topological charge happen to be closer than a critical distance, they attract each other. At first, they move very slowly; then, as the distance between them becomes less than a diameter, their relative speed increases dramatically, until they annihilate one other. In this paper we describe, by means of a simple dynamical model, the attraction and annihilation of two defects in an infinite tube. We write the balance between the rate of change in the elastic free energy stored within the interaction region and the energy dissipated in the director motion. Hence, we derive and solve the differential equation that describes the evolution in time of the distance between the defects. The outcomes of our analysis confirm many qualitative aspects of the experimental evidences.

THE DYNAMICS OF A PERIODIC ARRAY OF DEFECTS, G.Guidone Peroli and E.G. Virga, 1) Dipartimento di Matematica, Università di Pisa, 56127 Pisa, Italy; 2) Dipartimento di Matematica, Università di Napoli, 60125 Naples, Italy.

The topological theory of defects assigns a charge to every point defect exhibited by nematic liquid crystals. Complex phenomena have been observed in capillary tubes involving the appearance and the disappearance, along the axis of the tube, of periodic arrays of defects with

alternating sign of the charge. 1)

Here we develop a mathematical model fit to describe the evolution in time of these arrays and to explore their stability. We write the differential equations that rule this peculiar dynamical system: they show how a defect is dragged in the wake of another with a velocity which depends on the distance between them. Building upon this elementary phenomenon, we explain how an unstable array can reach a neutral configuration accommodating less defects at a greater distance from one another.

1) G.P.Crawford, M.Vilfan, J.W. Doane, and I. Vilfan, Phys. Rev A 43, 835 (1991)

D4P.14

THEORY OF SMECTIC A CHEVRON DYNAMICS, A.N. Shalaginov, L.D. flazelwood and T.J. Sluckin. Dept. of Mathematics, University of Southampton, Southampton SO17 1BJ, UK.

We present a theory of the dynamics of chevron formation in Smectic A liquid crystals confined to thin cells when the driving mechanism for the chevrone is elastic mismatch between equilibrium layer thickness in the bulk and at the surface. The theory uses the Kats-Lebedev formulation of smectic A dynamics. If hydrodynamics is neglected the driving force is a simple TDGL term, and the relexation times are of the order of hours. In the presence of hydrodynamic coupling, in which a body force from the smectic mean field is balanced by viscosity, this is reduced to seconds. The late time behavior goes as  $t^{-1}$ . Slowing down may occur in a closed system in which large scale hydrodynamic motions are suppressed. Extensions of the theory to Sm C chevron dynamics are discussed.

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† Work supported by (UK) EPSRC Grants GR/H68352.

**D4P.15** 

THERMAL ENTROPIC EFFECT AT THE ELECTRIC FIELD INDUCED ISOTROPIC-NEMATIC TRANSITION, <u>I. Lelidis</u> and G. Durand, Laboratoire de Physique des Solides, Bâtiment 510, 91405 Orsay Cedex, France

We demonstrate the existence of a reversible entropic thermal effect in nematic liquid crystals, when one increases (or let decay) the orientational ordering with an external electric field. The system, close to the isotropic nematic transition, is quantitatively described by a Landau-Khalatnikov model. We measure the orientational order parameter S dynamics by an optical method. We do observe heating and cooling using S as a transient thermometer. When cooling, metastable states can be created. One goes from a fast adiabatic regime towards a very slow diffusion limited regime creating, a thermal bottleneck.



RELAXATION FROM THE FIELD-INDUCED HOMEOTROPIC STATE OF CHOLESTERIC LIQUID CRYSTALS, D.-K. Yang, Z.-J. Lu and P. Palffy-Muhoray\*, Liquid Crystal Institute, Kent State University, Kent, OH 44242, U.S.A.

It is observed that when a cholesteric liquid crystal is initially in the field-induced homeotropic state, when the applied field is reduced, the relaxation depends on the bias field. We show that when the bias field is below  $E_{hp} = (2/\pi) \sqrt{K_{22}/K_{33}} E_c$ , where  $E_c$  is the critical field to untwist the helical structure, the liquid crystal relaxes to the planar state. This transition takes place in two steps: first from the homeotropic state to a transient planar state with a pitch  $P = (K_{33}/K_{22})P_o$  and then from the transient planar state to the stable planar state with the intrinsic pitch  $P_o$ . The transition from the homeotropic state to the transient planar state is realized through a conic helical structure and is a homogeneous transition with the transition time  $T_{hp} = (\gamma/K_{22})P_o^2$ . When the bias field is higher than  $E_{hp}$ , the liquid crystal relaxes to the focal conic state via a nucleation process with a transition time governed by the density of nucleation sites. These predictions are confirmed by experiments.

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### D4P.17

SOLITONS AND PATTERN FORMATION IN A NEMATIC LC IN A ROTATING MAGNETIC FIELD, Chun Zheng and Robert B. Meyer, The Martin Fisher School of Physics, Brandeis University, Waltham, MA 02254-9110, U.S.A.

We have built a computational model to study solitons and pattern formation in a nematic liquid crystal in a rotating magnetic field [1]. Based on this model, we can predict the speed of a dynamic soliton in response to the frequency of the rotating magnetic field. We discovered that there exists a critical frequency below which a soliton does not move. By incoporating the flow coupling, we can also explain the optics and other novel pattern phenomena found in our experiment.

[1] K. B. Migler and R. B. Meyer, PRL. 66, 1485 (1991).

### **D4P.18**

DIELECTRIC RELAXATION IN MIXTURES OF LIQUID CRYSTALS OF DIFFERENT MOLECULAR LENGTH, E.I.Rjumtsev, <u>A.P.Kovskik</u>, B.S.Saburov\*, R.M.Umurzokov\*, Institute of Physics of St.Petersburg University, St.Petersburg, 198904, Russia, \*Tajik Agriculture Institute Department of Physics, Dushanbe, 734017, Tajikistan.

The binary mixtures of strongly polar liquid-crystalline compaunds of different molecular length and weakly polar nematic were stadied. In the friquency range of a.c. electric field  $(10^2-10^5)$ Hz the dispersion of complex dielectric permittivities  $\epsilon_{\parallel}, \epsilon_{\perp}$  and  $\epsilon_{is}$  in nematic and isotropic phases were investigated. The dielectric spectra of  $\epsilon_{\parallel}$ , and  $\epsilon_{is}$  show the existance of two low frequency experimentally distinct dispersion regions, connected with rotation of the molecules of different length around their short axis. The temperature dependence of the relaxation times in nematic and isotropic phases were determined and the retardation factors of the components of the samples investigated were calculated. It was shown, that experimentally obtained and theoretically predicted relationships between the relaxation times and molecular size did not coincided. From the temperature dependence of the retardation factors values of the nematic potential barriers of each components of the mixtures were obtained.

DIELECTRIC RELAXATION IN LIQUID CRYSTAL MIXTURES(solutions)WITH COMPONENT MOLECULS OF DIFFERENT ASYMMETRY OF SHAPE.B.S.Saburov.R.M.Umrzak Taiik Agricultural University 734017,146 Rudaki pr.Dushanbe,Republik of Tikistan

In the paper the rezults of study of influence of chemical structure and asymmetry of molecules of substance on dielectric relaxation time  $\mathcal{T}_u$ .connected with dispersion of parallel component of dielectric permittivity  $\mathcal{E}_u$  ave given liquid crystal mixtures of component molecules with different asymmetry of shape were chosen as subjects of inquiry. It is established that Cole — Cole diagram considerably differ from Debye's one in cases of mixtures of liquid crystal substances unlike individual within the rende of low frequencies. When constructing aplot of  $\mathcal{E}_u$ , as a function of  $2nf\mathcal{E}_u^k$  (where  $\mathcal{E}_u^k$ —is imaginary part of dielectric permittivity. f—is frequency) it is established that relaxation of  $\mathcal{E}_u$ , can be characterized by three dipole mechanisms with appreciably different(by an ozer of magnitude greater) frequency areas of dispersion. It is shown in that relaxation time connected with rotation of molecule about short axis depends considerably move on the length of molecule than on degree of its asimmetry.

D4P.21

THE ORIENTATIONAL DYNAMICS OF THE ISOTROPIC-NEMATIC PRETRANSITIONAL EFFECTS BY NONLINEAR DIELECTRIC SPECTROSCOPY, <u>Przemysław Kędziora</u>\*, Jan Jadżyn\*, and Louis Hellemans\*\*, \*Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznań, Poland, \*\*Laboratory of Chemical and Biological Dynamics, University of Leuven, B-3001 Leuven, Belgium.

Electric field of the high intensity ( $E_0 \sim 10^5$  V/cm) applied to the reacting system causes a non-linear increase in electric permittivity ( $\Delta \epsilon > 0$ ) due to a shift of chemical equilibrium that favor the more polar partners of the reaction. This field induced increment of the electric permittivity, measured by alternating electric field of a small amplitude ( $E \sim 1$  V/cm), shows a relaxation in the frequency region dependent on the rate of the chemical process. We have shown that the non-linear dielectric spectroscopy can be useful to the kinetics studies of the nematogenic molecules aggregation processes near the isotropic-nematic phase transition. The non-linear dielectric effect (NDE) has been measured for isotropic hexylcyanobiphenyl (6-CB) and hexylcyclohexylisothiocyanatobenzene (6CHBT) in the frequency region of the electric field E from 100 kHz to 10 MHz. The relaxation of the NDE in this frequency region has been observed. The values of the parameters describing this relaxation (amplitude and relaxation time), measured as a function of temperature, show a strong pretransitional effect when approaching to the transition to nematic phase. This dynamic dielectric effect (observed for the first time) has been discussed in terms of the kinetics of nematogenic molecules aggregation.

D4P.22

SPONTANEOUS ACOUSTIC EMISSION (AE) AT THE PHASE TRANSITION IN SMECTIC, E.Axelrod, V.Bespalov, V.Dobrin, V.Kriouk, A.Kuzmin, V.Melechin, Dep. of Appl. Phys., Ural Technol. Academy, Ekaterinburg, 620032, Russia

We have investigated the AE resulted from fundamental processes of solid nucleation and growth during the spherulite crystallization of cholesterylnonanoate. It is established that detected AE current is nonuniform and consists in two components with distinct amplitude, temporal and frequency distributions of pulses. It is shown the low-amplitude ("kinetic") constituent is due to dilatation effect of sporadic formation of overcritical nuclei and their subsequent development through secondary nucleation. The high-amplitude ("dynamic") component is generated by nonstationary glide of edge dislocation walls at the interface. This moving is induced by alteration of interface local curvature and electrostriction deformation arising at pulsations of the spherulite growth rate [1]. To trim a randomizing factors action we have measured the AE during isothermal growth of single crystallization nucleus and discovered the relationship between fractal properties of AE current return map and tensor density of interface dislocations.

[1] E.Axelrod, V.Bespalov, V.Dobrin et al., Proc. of Acad. Sci. (Russia). 345, 320 (1995).



### 1D AND 2D FT-IR TIME-RESOLVED SPECTROSCOPY OF LIQUID CRYSTALS

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FT-IR time-resolved spectroscopy (FT-IR TRS) has opened up a new field of dynamic infrared spectroscopy. This paper describes the most recent advances in 1D TRS (5µs and 200ns time-resolved spectroscopy) and 2D TRS (frequency correlation spectroscopy: IR COSY) experiments and report the results of dynamic analysis of liquid crystal reorientational transition. . 1D and 2D FT-IR time-resolved spectroscopy applied to the study of electric field-induced reorientational transition of nematic and ferroelectric liquid crystals has revealed that the flexible alkyl chain appended to a core moiety undergoes a fast local motion in addition to the overall reorientational motion of the molecule as a whole. The principle of FT-IR TRS, experimental set-up, and examples of its application to other related subjects will be described.

### D4P.24

DIELECTRIC RELAXATION STUDY IN A GLASS-FORMING FERROELECTRIC LIQUID CRYSTAL WITH N\*-SmC\* PHASE SEQUENCE

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The dynamics of a new chiral oxazoline derivative [1] has been studied by means of broadband dielectric spectroscopy (10<sup>-2</sup> Hz-10<sup>9</sup> Hz). The phase transition sequence on cooling (I-BP-N\*-SmC\*-Sm1 (unidentified smectic phase)-glass shows a broad range of SmC\* phase with a high spontaneous polarization (300nC cm<sup>-2</sup>) and a strong Goldstone mode. The frequency of this mode and that of the mode related to the rotation around molecular long axis have a non-Arrhenius temperature dependence due to the influence of the glassy state.

[1] J.L. Serrano, T. Sierra, Y. González, C. Bolm, K. Weickhardt, A. Magnus, G. Moll, J. Am. Chem. Soc. **117**, 8312 (1995).

### **D4P.25**

BROADBAND DIELECTRIC SPECTROSCOPY IN CHIRAL GLASS-FORMING LIQUID

**CRYSTALS** 

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We report a broadband dielectric study (10<sup>-2</sup> Hz-10<sup>9</sup> Hz) of two new low-molecular-weight liquid crystals that undergo a glass transition. Both compounds are quiral, containing the naphtalene group in the core. The phase transition sequences are (compound I) I-SmA-glassy SmA and (compound II) I-N\*-glassy N\*. Several relaxations appear in the spectra. The temperature dependence of the frequency of the relaxation related to the rotation around molecular long axis does not show changes at the phase transitions. On the other hand, that of the relaxation related to the reorientation of long axis around short axis shows a jump at the I-SmA or I-N\* phase transitions. In both compounds the behavior is non-Arrhenius but following the Vogel-Fulcher-Tammann law.

HIGH PRESSURE DIELECTRIC STUDIES OF LIQUID CRYSTALS, T. Brückert +, S. Urban and A. Würflinger +; + Institute of Physical Chemistry II, Ruhr University Bochum, Germany; Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland.

The results of dielectric studies under high pressure of the cyano-compounds belonging to four homologous series (nCB, nOCB, nPCH and nCCH) will be presented. They concern the dielectric properties of the isotropic, nematic, smectic A and (monotropic) smectic B phases. The longitudinal relaxation times  $\tau_{\parallel}$  were obtained which allowed for calculations the activation parameters at isothermal ( $\Delta^{\bullet}V$ ), isobaric ( $\Delta^{\bullet}H$ ) and isochoric ( $\Delta^{\bullet}E$ ) conditions. These quantities show unusual behaviors when going away from the transition (isotropic - nematic or nematic - smectic) border lines. Additionally, the retardation factor  $g_{\parallel} = \tau_{\parallel}/\tau_{0}$  and the nematic potential q as functions of p, T and V were obtained. All the results will be discussed in frames of the known theories of the nematic state.

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**D4P.27** 

DYNAMIC ANALYSIS OF LIQUID CRYSTAL REORIENTATION BY USE OF POLARIZATION MODULATED ELLIPSOMETER, <u>T. Tadokoro</u>, T. Fukazawa, and H. Toriumi\*, Spectroscopic Instrument Division, JASCO Corporation, 2967-5 Ishikawa-cho, Hachiouji, Tokyo 192, Japan; \*Department of Chemistry, University of Tokyo, Komaba, Meguro, Tokyo 153, Japan.

Polarization modulated ellipsometry (PME) was applied to the study of liquid crystal reorientation dynamics. PME measures the wavelength dispersion of both phase difference and amplitude modulation ratio between p- and s-polarized lights, and thus provides information about complex refractive indices of continuously changing media. In addition to this capability of analyzing the depth profile, PME has several important advantages in studying liquid crystal reorientation dynamics, e.g., high speed data acquisition, high sensitivity in observing phase retardation (3 X 10<sup>-5</sup>) and wide wavelength range (260 - 860 nm). In this study, we applied the PME technique featuring a photo elastic modulator to the study of time and depth dependent variation of the orientational property of nematic 5CB molecules. Details of experimental setup, data processing and the results of analysis of 5CB reorientational dynamics will be reported.

D4P.28

STUDY BY PROTON AND DEUTERIUM NMR RELAXATION OF THE MOLECULAR DYNAMICS IN A DEUTERATED FERROELECTRIC LIQUID CRYSTAL, A. Ferraz<sup>1</sup>, J. L. Figueirinhas<sup>1</sup>, P. J. Sebastião<sup>1</sup>, A. C. Ribeiro<sup>1</sup>, F. Noack<sup>2</sup>, H. T. Nguyen<sup>3</sup>, <sup>1</sup>CFMC, Av. Prof. Gama Pinto, nº 2, 1699 LISBOA CODEX, PORTUGAL, and IST, Av. Rovisco Pais, 1096 LISBOA CODEX, PORTUGAL. <sup>2</sup> 4-Physikalishes Institut der Universität Stuttgart, (1205) Pfaffenwaldring 57, D-70550 STUTTGART, GERMANY. <sup>3</sup>CRPP, Domaine Universitaire, 33405 TALENCE, FRANCE.

We present a study of the molecular dynamics in the  $S_A$  and  $S_C^*$  mesophases of the liquid crystal  $C_8D_{17}O$ - $\Phi$ - $\Phi$ -OOC- $C^*HCl$ - $C^*HCH_3$ - $C_2H_5$  [1]. The proton spin-lattice relaxation times were recorded as a function of the temperature and the frequency (from 100 Hz to 300 MHz). Deuterium relaxation data were collected at 46 MHz as a function of the temperature. The simultaneous analysis of these two kinds of experimental results is presented, leading to a consistent understanding of the molecular dynamics in this compound. The results are compared with some previous works on this subject [2].

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STOCHASTIC MODELS FOR THE SPINNING MOTION IN BIAXIAL SMECTIC PHASES Mirco Wahab and Peter Schiller, Institut für Physikalische Chemie, Mühlpforte 1, 06108 Halle/Saale, Germany

The dielectric spectrum of an isotropic system yields only little information on the underlying stochastic process. Rather different stochastic models are associated with an exponentially decaying dipole-dipole autocorrelation function, which leads to a simple Debye-spectrum. In most cases a Brownian reorientation process is assumed, although other models would be also suitable to fit the experimental data. Measurments of dielectric constants referring to different directions in an anisotropic medium provide more information on the reorientation process. Especially, the splitting of the relaxation spectrum due to the biaxiality is suitable to distinguish between several stochastic models. Currently available experimental data for the smectic C phase allow a better fit by assuming a discontinuous reorientation process instead of the continuous Brownian motion [1].

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### **D4P.30**

STUDY OF ROTATIONAL DIFFUSION OF ASYMMETRIC MOLECULES IN LIQUID CRYSTALS USING DEUTERON SPIN RELAXATION, G. M. Richards and R. Y. Dong<sup>\*</sup>, Department of Physics and Astronomy, Brandon University, Brandon, Manitoba R7A 6A9.

We report on the measurement of deuteron Zeeman  $(T_{1Z})$  and quadrupolar  $(T_{1Q})$  spin-lattice relaxation times of the ring and  $C_{\alpha}$  deuterons in the mesophases of 4-n-butoxybenzylidene-4'-n-octylaniline (40.8) at 15.2 and 46 MHz. A new global target approach is used to analyze the spectral density data of 40.8 and the reported data [1] of 10.4. The word "global" means that spectral data at different temperatures are handled in the same fitting procedure, while the word "target" implies fitting some chosen parameters in a motional model. We apply the Nordio model and its extension [2] to asymmetric molecules to describe reorientations in liquid crystals. In the case of 40.8, director fluctuations are required in part for relaxing the deuterons. We discuss the usefulness of globally analyzing deuteron relaxation data for these liquid crystals.

- [1] R.Y. Dong, L. Friesen, and G.M. Richards, Mol. Phys. 81, 1017 (1994).
- [2] R. Tarroni and C. Zannoni, J. Chem. Phys. 95, 4550 (1991).
- \*Supported by the National Sciences and Engineering Council of Canada.

### D4P.31

DIELECTRIC BEHABIOR OF SEMIFLUORINATED N- ALKANE,II,K.Araki\*, K.Satoh, and S.Kondo, Department Material Science and Engineering, Science University of Tokyo in Yamaguchi, Onoda,Yamaguchi 756, JAPAN

We have investigated and reported on dielectric behavior of semifluorinated n-alkane  $(F(CF_2)_n(CH_2)_mH)$ , (n,m)=(10,10) and  $(12,8)^1)$ . These results lead to conclusion that there is a difference in the rotational motion of the  $(CF_2)$  group in F10H10 and F12H10. In this works, we will discuss the relation between dielectric relaxation behavior and the chain length of semifluorinated n-alkane,i.e.  $n=10,m=7\sim14$ , respectively.

Dielectric measurements were carried out over the frequency range 20 Hz to  $1 \times 10^6 \text{ Hz}$  with computed controlled HP4284A Precision LCR meter and made in the temperature range from the solid to isotropic state.

[1] K.Araki, K.Satoh and S.Kondo, Mol. Cryst. Liq. Cryst., in press.

MEASUREMENTOF ELECTROMECHANICAL COUPLING COEFFICIENT OF A CHOLESTERIC SAMPLE UNDER HOMEOTROPIC ANCHORING, S. Thiberge, L. Gil, J. M. Gilli, I.N.L.N., CNRS UMR 129, 1361 Rte des Lucioles, 06560, France.

Quantitative experimental measurements of the drift velocities are done on the localized structures appearing under homeotropic conditions with cholesteric liquid crystal samples. This drift induced by application of dc voltage perpendicular to the glass plates is associated to the so called electromechanical coupling phenomena (1, 2).

The experimental measurements associated to computer calculations (2) derived from Franck energy formula for cholesteric liquid crystals allows us to derive values of this coefficient.

1)N. V. Madhusudana, R. Pratibha, Mol. Cryst. Liq. Cryst. Lett, 5, 43, 1987. 2)J. M. Gilli, L. Gil, Liq. Cryst., 17, 1, 1994, T. Frisch, L. Gil, J. M. Gilli, Phys. Rev. E, 48, R4199, 1993, L. Gil, J. Phys. 2, France, 5, 1819, 1995.

D4P.33

ELECTROCONVECTIVE INSTABILITIES IN BOUND AND FREELY SUSPENDED NEMATIC LAYERS, K. S. Krishnamurthy, and R. Balakrishnan, Applied Science Department, Faculty of Electrical and Mechanical Engineering, College of Military Engineering, Pune, 411031, INDIA.

EHD effects due to a low frequency transverse field have been previously reported [1] for a bound nematic slab of high conductivity MBBA, in which the initial director pattern is homeotropic at the limiting surfaces and contains a -1/2 disclination loop. In an extension of this study, both bound and freely suspended films have now been examined at various field frequencies. The orientational distortion generally originates as two periodic waves at the disclinations parallel to the electrodes, and the pattern symmetry is determined by their relative phase difference. For bound samples, the waves are always in phase, resulting in non-centrosymmetric domains. For freely suspended films, both inphase and 180° out of phase waves occur with the domains being centrosymmetric in the latter case. In bound samples, close to cut-off frequency, two oppositely drifting wave-trains appear along the electrode edges. Focal powers of liquid crystal lenses, secondary instabilities leading to turbulence and frequency-dependence of pattern are among the other aspects studied.

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D4P.34

FREQUENCY DEPENDENCE OF THRESHOLD IN BEND FREEDERICKSZ GEOMETRY OF 4-N-PENTYL-4-CYANOBIPHENYL

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U. D. Kini, Raman Research Institute, Bangalore, India.

We report the effect of electric frequency on deformation threshold in the bend Freedericksz geometry in the presence of a stabilizing magnetic field applied normal to the plates with the destabilizing electric field impressed parallel to the sample. In general, the observed threshold and deformation above it are strongly dependent on frequency and magnetic strength associated with a pretransitional field-induced biaxiality. The periodic deformation observed under a strong magnetic field has wavevector along the electric field at low frequencies. Above a cut-off frequency, the direction of the wavevector becomes normal to the electric field. The hysterisis between increase and decrease of voltage is noticeable. A homogeneous deformation is observed under weak magnetic fields and high frequencies. At dc or low frequency excitation, there is clear evidence of hydrodynamic flow which can become turbulent for some values of parameters. A qualitative theoretical discussion is provided for some of the observations.

<sup>\*</sup>Supported by NSF REU grant DMR 9322301



QUASIPERIODIC STRUCTURES IN THE REGION OF NEMATIC-ISOTROPIC PHASE TRANSITION, V.F.Kitaeva and A.S.Zolot'ko. P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Leninsky pr.53, Moscow, 117924, Russia

The phase separation and appearence of drops of isotropic phase were observed in multicomponent mixtures of nematic liquid crystals at the crystal temperature being higher than the temperature at the lower limit of the temperature interval of the diffuse phase transition [1]. The drops form quasiperiodic structure under the influence of the forces acting between them due to the deformations of initially homeotropic director field.

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### **D4P.36**

Laser Induced Configurational Transition In Dye-doped Liquid Crystal, G. Hu, P. Palffy-Muhoray, Liquid Crystal Institute and Department of Physics, Kent state University Kent OH 44242,USA

We have investigated the reorientation of NLC in thermal gradient field. We observed the temperature gradient induced LC director reorientation. The nonuniform temperature field was produced by focusing He-Ne laser no a dye doped homeotropiclly aligned NLC cell. A simple model is proposed, where the reorientation is resulting from the coupling of flexo-electric effect and the DC electric field induced by order-electric effect. The predictions of the model are compared with the results of experiment on dyed nematics. The theoretical threshold temperature gradient for director reorientation is comparable with experimental value. The calculation of free energy shows this configuration transition is second order. The effects of director reorientation on absorption and on the far field diffraction pattern are also discussed. The reorientation induced by angular momentum of light field in dye doped NLC is also observed.

### **D4P.37**

MOLECULAR ALIGNMENT WITHIN THE STRIPE DOMAINS OF AN ELECTROCLINIC LIQUID CRYSTAL, J. R. Lindle, S. R. Flom, F. J. Bartoli,, A. Harter, R. E. Geer, B. R. Ratna, R. Shashidhar, Naval Research Lab, Washington, DC, 20375.

Electroclinic liquid crystals frequently exhibit stripe domains due to the field induced deformation of the bookshelf geometry. The nature of these stripe domains has been investigated using a novel, spatially-resolved, optical technique which permits measurement of the birefringence, optical tilt angle and extinction within a single stripe domain. A comparison of these results with previous X-ray data<sup>1</sup> and standard optical measurements allows us to extract information on the molecular alignment within a stripe domain. Modeling of the results shows that the picture of a triangular deformation with uniform alignment within a stripe is probably naïve, and that the optical response is dominated by substructure within the stripe domains.

[1] G. P. Crawford, R. E.Geer, J. Naciri, R. Shashidhar, and B. RRatna, Appl. Phys. Lett. 65, 2937 (1994).

ELECTRIC FIELD INDUCED PATTERN FORMATION IN LIQUID CRYSTALS AND THE DEPENDENCE ON MATERIAL PARAMETERS, <u>G. Hauck</u>, H. D. Koswig, and U. Labes, Iwan-N.-Stranski-Institut, Technische Universität Berlin, Hausvogteiplatz 5-7, D - 10117 Berlin, Germany

In free-standing films of ferroelectric liquid crystals systems of dark and bright rings can be spontaneously created by a rotating electric field. This pattern formation depends on the parameters of the applied field [1]. We have investigated the dependence of the ring creation on material parameters (pitch, rotational viscosity, spontaneous polarisation) and on the temperature. The rotational viscosity is the most important parameter for the temperature dependence of the structure formation. The qualitative correspondence between the experimental results and a simulation which is based on the theoretical description of this pattern formation [2] is quite well. For low frequency and high field strength a circular flow occurs in free-standing films. Our measurements give rise to the assumption that the spontaneous ring creation is not caused by this flow, but by the phase delay between field rotation and director motion as shown theoretically [2]. The pattern formation in rotating electric fields is not restricted to free-standing FLC-films, but could be observed also in other experimental arrangements, e.g. in films of non-chiral smectic phases or in homeotropically aligned nematic cells.

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[2] A. Kilian, H. D. Koswig, and A. Sonnet, Mol. Cryst. Liq. Cryst. 265, 321 (1995).

D4P.39

FORMATION AND DYNAMICS OF CONVECTIVE PATTERN IN HOMEOTROPIC SYSTEM OF NEMATIC LIQUID CRYSTALS, Y. Hidaka, K. Hayashi and S. Kai, Department of Applied Science, Kyushu University, Fukuoka, 812-81, Japan

We have experimentally investigated the electrohydrodynamics in homeotropically oriented nematic layers with negative dielectric anisotropy. Especially we observed the pattern formation and dynamics, and have obtained three results so far. First, we obtained the phase diagram of the convective patterns for the applied voltage and frequency in order to classify the patterns in homeotropic case. Magnetic field  $H=1600\mathrm{G}$  was applied to the convective system in order to suppress the Goldstone mode. The second result is the Busse diagram under  $H=1600\mathrm{G}$ . We discovered the new instability that the Eckhaus instability occurs first, and zig-zag instability is followed at once. Thirdly, we investigated the bifurcation to spatio-temporal chaos, that is, weak turbulence. As a result, we found that the spatio-temporal chaos of the convective pattern with H=0 occurs directly from a spatially uniform state with no convection, which is different from the planar case.

D4P.40

PATTERN FORMATION OF THE CHOLESTERIC FINGER UNDER THE MAGENETIC FIELD, Tomoyuki Nagaya, Y. Hikita, H. Orihara and Y. Ishibashi, Department of Applied Physics, School of Engineering, Nagoya University, Nagoya 464-01, Japan.

It is known that the cholesteric finger pattern appears in a large pitch cholesteric liquid crystal sandwiched between glass plates with homeotropic anchoring[1]. In the present study, the effect of magnetic field on the growth of the cholesteric finger pattern has been investigated experimentally. It is found that, under the magnetic field, whose direction is perpendicular to the glass plates of the cell, the cholesteric finger grows up toward the direction of the magnetic field. In addition, the velocity of the finger is accelerated by the magnetic field.

In order to analyze the experimental results, we performed a numerical simulation. Consequently, the characteristic features of the growth of finger pattern can be reproduced by the simulation.

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PREFERRED EQUILIBRIUM SHAPES OF SMECTIC A PHASE GROWN FROM ISOTROPIC PHASE, <u>H. Naito</u> and Z. Ou-Yang\*, Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka, Japan, \*Institute of Theoretical Physics, Academia Sinica, P. O. Box 2735, Beijing 100080, China.

We have described a theory for preferred equilibrium shapes of smectic-A (Sm-A) phase grown from isotropic phase, and have derived the general shape equation by minimizing the nucleation energy of Sm-A phase [1]. The general shape equation predicts the existence of equilibrium toroidal structures. We have experimentally demonstrated this prediction in the binary mixtures of octyloxycyanobiphenyl with dodecyl alcohol. We have further shown that such tori can be regarded as a seed of focal conic domains (FCD), and in addition that the conformal invariability of the general shape equation reveals that Dupin cyclides can also be regarded as a seed of FCD. The conformal invariability further gives an explanation for the key characteristics of FCD's; the size of FCD's is distributed to fill space.

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### **D4P.42**

PATTERNS ON THE NEMATIC-SMECTIC-B INTERFACE OF BINARY MIXTURES AND THE INFLUENCE OF THE THERMALLY FORCED AGEING IN ONE-COMPONENT SUBSTANCES T. Tóth Katona, N. Éber and Á. Buka, Research Institute for Solid State Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B.49, Hungary

Patterns on the  $N-S_B$  interface in binary mixtures of a homologous series with different concentrations has been studied. Varying the concentration morphologies of the interface, such as dendritic (with four mainbranches, enclosing an angle of  $90^{\circ}$ ), dendritic-like (with asymmetric tips) and faceted shapes have been observed. Similar morphologies have been seen in different one-component substances of the homologous series. Strongly decreased growth velocities and weaker side-branching activity (large wavelength, slow growth without second generation of the side-branches) have been found in the mixture compared to that in one-component substances. Similar effects in the pattern forming behaviour could be also generated by keeping the one-component sample in the N phase for a long time (several days). The changes have also been accompanied with the decrease of the phase transition temperature and with the increase of the temperature range of phase coexistence, which could indicate the presence of impurities. Unexpectedly, the samples could be partly recovered from these changes after several heating-cooling cycles, that might suggest a reversible change of the molecular conformation.

### **D4P.43**

GROWTH OF BANDED SPHERULITES IN A LIQUID CRYSTAL, Jeffrey L. Hutter and John Bechhoefer, Department of Physics, Simon Fraser University, Burnaby, B.C., Canada.

A single material can solidify in several distinct forms, depending on the undercooling. Dendritic growth, which occurs at low undercooling, has been intensively studied, as has the glass transition, which occurs at high undercoolings where the viscosity of the melt becomes very large. At intermediate undercoolings, one often sees a variety of ordered forms which are not well understood. An example is spherulitic growth, in which spherical, polycrystalline aggregates are formed. Although this growth mode has been studied in materials as diverse as elemental selenium, biomolecules, and polymers, there is no generally accepted theory. In particular, the cause of the concentric banding seen in many spherulites remains a mystery. We have studied banded spherulitic growth in a liquid crystal. Video-rate microscopy shows that microcrystals nucleate in the smectic A phase at the spherulite surface and expand laterally in bands. Atomic-force images reveal that the bands are associated with a periodic modulation of the density of microcrystals. We find no evidence for the periodic branching or the helical twist of the microcrystal orientation that are typically seen in polymeric systems. These findings have implications for any general theory of spherulitic growth that would explain the mechanism of this growth modes in all of the systems in which it is observed.

DENDRITIC GROWTH OF ELECTROHYDRODYNAMIC CONVECTION, J.T. Gleeson, Dept. of Physics and Astronomy, The University of Calgary, Calgary, AB, T2N 0S9, Canada

The transition to electrohydrodynamic convection when there is a strong magnetic field parallel to the applied electric field is strongly subcritical. If this system is abruptly displaced from equilibrium, the convection state invades the Freedericksz distorted state via the well-known dendritic growth mechanism. We have measured the tip speeds and tip curvatures of these dendrites and find remarkable agreement with the two-dimensional Ivantsov solution for needle crystals in the absence of surface tension. The observed dendrites have Péclet numbers varying by a factor of forty. The field controlling this growth morphology is apparently the diffusion of nematic director orientation.

D4P.45

ACOUSTIC RADIATION (AR) AT THE NEMATIC ELECTROCONVECTION, E.Axelrod, V.Dobrin, V.Kriouk, O.Lykova, A.Kuzmin, Department of Applied Physics and Biophysics, Ural Technology Academy, Ekaterinburg, 620032, Russia

It is established the large scale spatial evolution of MBBA roll pattern during dc voltage convection in sandwich cell with significant aspect ratio is succeeded by AR bursts generation. Based on AR spectrum and central moments dependences on overcriticality parameter it is shown, that detected AR has dipole origin resulted from the vortice velocity oscillations. Using Poincare and return maps technique for the AR time series data we have estimated attractor dimensions, largest Lyapunov exponents and Heurst coefficients vs degree of overcriticality and discovered in particular intermittency of "chaos - chaos" type between dynamic scattering modes. The correlation between multifractal structure of dissipation field for turbulence energy within inertia gap and chaotic dynamic of disclination loops in fully developed turbulence regime is discussed. In conclusion we have carried out the comparision with results were obtained by optical methods in relation to convection in isotropic liquid [1] and phase transition of first order [2].

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- [2] S.Kai, W.Zimmerman, M.Andoh, N.Chizumi, Phys. Rev. Lett. 64, 1111 (1990).

**D4P.46** 

THE NEMATIC'S DIRECTOR FLUCTUATIONS IN A FINITE THICKNESS SLAB IN THE EXTERNAL ELECTRIC FIELD, <u>A.N.Chuvyrov</u>, N.G.Migranov, A.V.Verevochnikov, Physic Department, Bashkir State University, 450074, Ufa, Frunze str.32, RUSSIA.

We have investigated the director's correlation function of the nematic liquid crystals in the finite thickness cell in the d.c. external electric field presence. By use of the theory of the quasistationary fluctuations [1], the director fluctuations' spectral representation in the d.c. external electric field was written out. The spectral representation does not take account of electroconvection process and consist of two Lorentzian curves superposition. In the electric field absence the correlation function reduces to one that well known [2].

- [1] L. Landau, Ye. Lifshitz, Theoretical Physics. Statistical Physics, vol. 10, Nauka, Moscow, (1978).
- [2] Orsay group, J.Chemical Physics 51, 816 (1969).



HARD MODE ONSET OF DOMAIN OSCILLATION, V.A. Delev, O.A. Scaldin, A.N. Chuvyrov, E.S. Batyrshin, Department of Physics, Bashkir State University, Ufa 450074, Russia.

The properties of nonstationary domain structure observed in the planar nematic liquid crystal cell in dc electric field above the electrohydrodynamic convection (EHC) threshold have been experimentally investigated. When a stationary two-dimensional grid pattern (GP) loses its stability, the stochastic auto-oscillation of domains occurs suddenly by jump, so that no any domain oscillation are observed with frequency less than some threshold frequency  $f_c$ . In particular, for MBBA the onset frequency of domain oscillation was obtained to be equal 0.15 Hz (h=20  $\mu$ m, U<sub>c</sub>=9.2 V) and then one increases lineary with applied voltage. Thus, onset of stochastic auto-oscillation by the jump confirms an existence of hard mode instability in the EHC-system.

### D4P.49

THE TEMPERATURE-INDUCED ORIENTATIONAL TRANSITION AND NONLINEAR PIEZOELECTRICAL EFFECT IN NEMATIC LIQUID CRYSTALS, Khazimullin M.V., Scaldin O.A., Lebedev Y.A., Chuvyrov A.N., Institute of Physics of Molecules and Crystals, Ufa Research Center, Russian Academy of Sciences, Ufa 450025, Russia.

The nonlinear piezoelectrical effect in the thin planar and homeotropic nematic liquid crystal (NLC) layers has been investigated. The NLC layers were deformed by periodical excitation of upper substrate. It has been found that the temperature behavior of piezoelectrical response  $U_{i\omega}$  at the dual excitation frequency near clearing point is essentially critical. The existence of piezosignal at the dual excitation frequency was suggested to be connected with the orientational instability of surface polarization layer  $P^s$ . By using polarized optical microscopy it has been established that the director changes orientation from planar to homeotropic in vicinity of phase transition point. The temperature dependence of director tilt angle ( $\theta$ ) are determined from data of birefringence measurements.  $\theta(T)$  and  $U_{i\omega}(T)$  were used for calculation of surface polarization  $P^s(T)$ .

### D4P.50

PROPERTIES OF TRAVELLING WAVES IN THE ELECTROCONVECTION OF A NEMATIC, Á. Buka<sup>†</sup>, N. Éber<sup>†</sup>, L. Kramer<sup>‡</sup>, M. Treiber<sup>‡</sup>, <sup>†</sup> Research Institute for Solid State Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B. 49, Hungary, <sup>‡</sup>Universität Bayreuth, Theoretische Physik II, Universitätstr. 30, D-95440 Bayreuth, Germany

Travelling rolls are a special form of the electrohydrodynamic instability appearing in particular near the cut-off frequency of the substance. We have studied the phenomenon in a mixture (Nematic Phase 5, Merck) by digital image processing techniques. The ac frequency dependence of three basic parameters (the threshold voltage, the wavelength of the pattern and the frequency at threshold) for cells with different thicknesses. Experimental data have been compared with the predictions of the recently developed weak electrolyte model [1]. To help theoretical modeling we measured some material parameters (elastic moduli, anisotropy of electric conductance, etc.) of the substance using the classical techniques of electric and magnetic Freedericksz transitions.

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STABILITY OF UNDULOIDLIKE SHAPES OF SMECTIC-A PHASE GROWN FROM ISOTROPIC PHASE, Y. Hirose, H. Naito, and Z. Ou-Yang \*, Department of Physics and Electronics, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka, Japan, \*Institute of Theoretical Physics, Academia Sinica, P. O. Box 2735, Beijing 100080, China.

Smectic-A (Sm-A) phase appears in variety of shapes on cooling the high temperature isotropic (I) liquid phase. One of the interesting shapes is a cylinder structure with beaded configuration [1]. We have developed a theory for equilibrium shapes of Sm-A nuclei grown from I phase [2] and have suggested that the cylinder structure can be described by unduloid in Delaunay's surfaces [3]. In this presentation, we discuss the stability of the unduloidlike shapes of Sm-A phase in light of the static theory, and compare the present theoretical results with our experimental results in the binary mixture of octyloxycyanobiphenyl with dodecyl alcohol.

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D4P.52

ORDER-CHAOS TRANSITION IN ELECTROCONVECTION IN HOMEOTROPIC NEMATICS, P. Tóth †, A. Rossberg†, L. Kramer† and A. Buka‡ † Physikalisches Institut der Universität Bayreuth, D-95440 Bayreuth, † Res. Inst. for Solid State Physics of the Hungarian Academy of Sciences, H-1525 Budapest, P.O.B.49, Hungary

Electroconvection in homeotropically aligned nematic LCs exhibits a wide range of pattern forming phenomena. Convection usually sets in as a secondary instability after the bend Freédericks-transition, which spontaneously breaks the rotational symmetry in the plane of the nematic layer. Due to the coupling of the convective mode and the Goldstone mode resulting from the broken symmetry a direct transition to spatio-temporal chaos occurs under very general conditions. Ordered patterns reappear when applying a magnetic field perpendicular to the initial director alignment. Choosing this field sufficiently small the transition from order to chaos can be shifted arbitrarily close to the onset of convection, which allows a quantitative comparison of theory and experiment. We investigated the stability of roll-patterns and characterized the chaotic state in particular by its defect dynamics.

D4P.53

PASSAGE-TIME STATISTICS FOR THE FREEDERICKSZ TRANSITION IN NEMATIC LIQUID CRYSTALS, Peng-Ye Wang, CCAST (World Laboratory) P.O.Box 8730, Beijing 100080, China and Institute of Physics, Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, China\*

A new statistical investigation of the Freedericksz transition in nematic liquid crystals is presented. After applying an external field that is exceeds the critical value to a nematic liquid crystal, the system relaxes from a stochastic initial state determined by the internal fluctuation of the nematic director. Detailed theoretical analyses is given for this decaying process with a two-stage consideration. The two stages are separated by comparing the variance of the time-dependent distribution of the director to that of the steady-state distribution at the critical point. The first stage is considered as an Ornstein-Uhlenbeck process while the second stage as a nonlinear deterministic transformation of the first stage in the derivation of the first-passage-time distribution function. Monte Carlo simulations show that the present theory describe the system much better than the previous asymptotic analysis.

This research was supported by the National Natural Science Foundation of China.

\*Mailing address

ELECTROHYDRODYNAMIC CONVECTION IN NEMATICS DRIVEN BY STOCHASTIC FIELDS H. Amm, U. Behn, and R. Stannarius, Universität Leipzig, Fakultät für Physik, 04103 Leipzig, Germany Electrohydrodynamic convection (EHC) in nematic liquid crystals is an extensively studied phenomenon. It provides a convenient and easily manageable system for investigations of dissipative pattern formation. Theoretical [1] as well as experimental [2] efforts have been devoted to the problem of noise excitation of EHC in the past, but a quantitative understanding of some observed phenomena still lacks. We study planar nematic cells driven by stochastic electric fields and superimposed waveforms. Optical transmission textures are observed microscopically, and quantitatively characterized by digital image processing. A variety of dissipative patterns is found under noise excitation. Transition from the uniform state to DSM occurs via non-stationary fluctuating states. We determine threshold curves for the onset of convection and construct stability diagrams. Results are compared to theoretical predictions of a stability analysis of the coupled stochastic differential equations describing the system to eluciate the mechanisms involved in

the dissipative pattern formation process.
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### D4P.55

SURFACE STATES, TRAVELING WAVES AND TOPOLOGICAL TURBULENCE DUE TO MAGNETIC INTERACTIONS IN ELETROHYDRODYNAMIC CONVECTION, J. P. McClymer, H. Shehadeh and E. F. Carr, Department of Physics and Astronomy, University of Maine, Orono, ME 04469-5709, USA.

A stabilizing magnetic field applied to MBBA undergoing electrohydrodynamic convection in the conduction regime produces some new phenomena. The magnetic field stabilizes traveling waves (TW) which can be observed over a large frequency and voltage range. The TW consist of large regions flowing parallel to the magnetic field with adjacent regions flowing in the opposite direction. The regions are separated by four defect lines which serve as nucleation sites for disclination loops leading to DSM 2. Observation of these regions with the removal of the electric field show the ability to rotate the plane of polarization of obliquely incident light which we interpret as due to surface bend-splay walls. The connection of these walls to the TW state will be presented. The dynamic scattering states consist of disclination loops which decay upon removal of the electric field. This decay is compared to theoretical predictions. While the form of the equation gives good fits the value of the coefficients are not as expected.

1. H. Toyoki and K. Honda, Prog. Theor. Phys. 73, 237, (1987), .M. Mondello and N. Goldenfeld, Phys. Rev. A, 45, 657 (1992); Phys. Rev. A, 42, 5865 (1990).

### **D4P.56**

DISSIPATIVE PATTERNS OF NEMATICS DRIVEN BY A ROTATING MAGNETIC FIELD M. Grigutsch, and R. Stannarius, Universität Leipzig, Fakultät für Physik, 04103 Leipzig, Germany Nematic liquid crystals (NLC's) driven far from equilibrium by a continuously rotating magnetic field provide a mechanical model for excitable media. Control parameters can be easily adjusted and arising patterns are observed by polarizing microscopy. The system is particularly well suited to study the properties of periodically generated transient structures. Among the various types of dissipative patterns generated in this system as for example circular and linear phase waves and solitary waves, stripe patterns and non-regular complex textures [1], we concentrate primarily on periodically amplified transient stripe textures formed in the asynchronous reorientation regime of a thin homeotropic NLC layer.

We report results of optical investigations. By means of digital image processing, transmission textures are quantitatively characterized. Wavelengths, dynamics and existence ranges of the patterns are determined. A theoretical model is developed for the amplification of thermal fluctuation modes. The model incorporates hydrodynamic backflow coupling and considers the important role stochastic noise in the evolution of the patterns. It describes correctly the dynamical evolution, wave lengths and orientations of the observed textures and provides insight in the mechanisms of transient pattern formation.

[1] Migler, K.B.; Meyer, R.B. Phys. Rev. Lett. 66 1485 (1991), Phys. Rev. E 48 1218 (1993).

DIRECTOR FIELD PATTERNS OF NEMATIC POLYMER SOLUTIONS AT ASYNCHRONOUS ROTATION IN A MAGNETIC FIELD, E. Pashkovsky\*, W. Stille, G. Strobl, D. Talebi, Fakultät für Physik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany.

A variety of different patterns is observed when a magnetic field **B** rotating with an angular frequency  $\omega$  is applied on a nematic cell with homeotropic boundary conditions [1]. To study the role of backflow in the formation of these dissipative structures, we compared the behavior of dilute solutions of a mesogenic side group polymethacrylate in a low molar mass nematic liquid crystal (5CB) with that of the pure solvent. In the obtained state diagrams dissolved polymer molecules lead to a strong reduction of the existence range of the the so-called VRL-TI (viscosity reduction lattice transverse instability) and complex states. For mass fractions w > 2% of the polymer these states were found to be suppressed completely due to the efficient reduction of backflow. The growth rate of the viscosity reduction lattices, which can still be observed, is in addition dependent on the polymer concentration. For completely suppressed backflow (and in absence of phase lag sources) numerical calculations resulted in a negative growth rate for lattices with finite lattice period.

[1] K. B. Migler, R. B. Meyer, Phys. Rev. Lett. 66, 1485 (1991); Phys. Rev. E48 (1993) 1218. \*Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi pr. 31, St. Petersburg, Russia

D4P.58

SLOW DIRECTOR OSCILLATIONS IN NEMATICS UNDER OSCILLATORY FLOW, A. P. Krekhov, and L. Kramer, Institute of Physics, University of Bayreuth, D-95440 Bayreuth, Germany

The orientational behavior of a nematic liquid crystal layer under plane oscillatory Couette and Poiseuille flow has been investigated theoretically. It is shown that for boundary conditions (strong surface anchoring) coinciding with the flow alignment angle  $(\tan^2\theta_{fl}=\alpha_3/\alpha_2)$  the director orientation at  $\theta_{fl}$  is stable with respect to small perturbations in the flow plane at all amplitudes of low-frequency oscillatory Couette flow. By contrast, for oscillatory Poiseuille flow, there is a critical amplitude above which the solution  $\theta=\theta_{fl}$  becomes unstable. We find that under Poiseuille flow and with appropriate alignment conditions by surface anchoring and/or magnetic field a state with slow, spontaneous director rotation appears. A slow time-periodic director motion appears with increasing amplitude of low-frequency Poiseuille flow through a homoclinic bifurcation and disappears through a Hopf bifurcation. The effect depends strongly on the anisotropy of elastic constants and in fact disappears in the one-constant approximation.

**D4P.59** 

THE SHEAR INDUCED DIRECTOR REORIENTATION IN NEMATICS, Scaldin O.A., Baimakova O.A., Chuvyrov A.N., Physics Department, Bashkir State University, Ufa, 4500074, Russia.

The orientational instabilities induced by oscillatory shear of thin homeotropic layers of nematic liquid crystal (NLC) have been investigated experimentally. NLC was sandwiched between two glass plates. A thin glass slide as a vibrator was located just symmetrically between these plates and was allowed to be oscillated with, frequency 20-5000 Hz and amplitude 0-200  $\mu$ m. In this geometry, two threshold effects were found: (i) the formation of stationary director inclination  $\theta$  within the shear plane and (ii) the azimuth al instability of director, when director goes out of initial shear plane (XZ) and begins moving upon an elliptical trajectory. The orientational director fluctuations in the vicinity of thresholds have been studied. It has been established that under oscillatory shear at f=190 Hz the low-frequency (<10 Hz) fluctuation modes are developed. These modes determine the character and dynamics of director reorientation.

[1] O.A.Baimakova, O.A.Scaldin, A.N.Chuvyrov, Mol. Cryst. Liq. Cryst. B265, 299 (1995).

LIGHT INDUCED INSTABILITIES IN BULK Sm-A LIQUID CRYSTAL †

Tatiana A. Krentsel (Lobko), Abed Ali, Oleg D. Lavrentovich, and Satyendra Kumar, Department of Physics and Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA.

The smectic-A phase of 8CB doped with a photosensitive azo compound has been reported [1] to exhibit unique structural changes and layer undulation instability upon exposure to UV or low level visible radiation. It is believed to be caused by light induced trans-cis and cis-trans isomerization of the dopant photosensitive molecules resulting in a change in smectic layer spacing. Our high-resolution x-ray scattering study of this phenomena in a mixture of 7AB (9.6 wt %) and 8CB at different temperatures in the smectic phase reveals that the exposure to UV light changes layer spacing by as much as 0.8%. The dynamics of such changes has a characteristic time comparable to the relaxation time of trans-cis isomerization.

[1] W. R. Folks, Y. A. Reznikov, L. Chen, A. I. Khizhnyak, and O. D. Lavrentovick, Mol. Cryst. Liq. Cryst. 261, 259 (1995)

† Work supported by NSF Science & Technology Center ALCOM grant DMR-89-20147.

### D4P.61

DOMAIN STRUCTURES IN FERROCHOLESTERIC LIQUID CRYSTALS, A.N.Zakhlevnykh and P.A.Sosnin, Physical Department, Perm State University, 614600 Perm, Russia

Continuum theory is used to analyze the effect of an applied magnetic field on the deformation of a ferrocholesteric spiral structure. The solid phase of a ferrocholesteric consists of single - domain needle - like ferromagnetic grains incorporated into cholesteric matrix. Homeotropic boundary conditions on the surfaces of the magnetic particles and positive diamagnetic anisotropy of the matrix are assumed. In this case the dipolar and quadrupolar mechanisms of orientational interactions compete with each other, tending to rotate the director in the opposite direction. The possibility of the field induced ferrocholesteric – ferronematic phase transition (helix unwinding) is discussed. The dependence of the transition field on the material parameters is found. Two competitive mechanisms of orientational behavior of a ferrocholesteric lead to arising of some features of the ferrocholesteric behavior under the applied field, in particular, the ferrocholesteric may exhibit domain structures with different orientation of the director at the quadrupolar and dipolar regimes. Our results show that in order to decrease the value of operated field, the dipolar orientational mechanism has to predominate over the quadrupolar one. Attention is paid to the dipolar regime of unwinding of the ferrocholesteric spiral structure and to the effect of grain redistribution under applied field. The average magnetization of the sample and magnetic susceptibility as a functions of a field are also determined.

### D4P.62

PROPERTIES OF MONODISPERSE LIQUID CRYSTAL EMULSIONS, P. Poulin, H. Stark, T.C. Lubensky and D.A. Weitz, Dept. of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104

We explore the properties of emulsions of thermotropic nematic liquid crystals in water. The droplets can be purified to be monodisperse, and the anchoring conditions of the liquid crystals can be controlled by varying the surfactant. In addition, smaller water droplets can be introduced within the larger liquid crystal emulsion droplets. By controlling the boundary conditions at the surface of both the larger and smaller droplets, defects can be introduced into the liquid crystalline phase, and the interactions between them can be observed. Strong elastic interactions are observed when the liquid crystal molecules are aligned normal to the interfaces; the small internal water droplets are attracted to one another, but a repulsive interaction persists at short ranges. These interactions play an important role in stabilizing the water droplets against coalescence. A simple picture is proposed to qualitatively account for these effects in terms of the interactions between the defects introduced by the presence of the droplets. In addition, the electro-optic response of the larger monodisperse liquid crystal droplets to an applied electric field is discussed.

PECULIARITIES OF INTERACTION BETWEEN THE RADIAL AND HYPERBOLIC POINT DEFECTS IN NEMATICS: CREATION AND DECAY OF THE CYLINDRICAL DEFECT

 $P_{+2}^c$ , T.V.Kushnareva, S.V.Kushnarev and V.K.Pershin\*, Department of Physics, Cheliabinsk State University, 454136 Br.Kashirin str., 129, Cheliabinsk, Russia

In the framework of continuum theory of nematics we have investigated how the radial (R) and hyperbolic (H) point defects interact with each other. The force of interaction is shown not to depend on the distance, but, as well as the result of coalescence of the defects, it is only controlled by their initial mutual orientation. Two limiting cases of mutual orientation have been considered, namely when symmetry axes of the defects are: 1) in line (the elastic field with axial symmetry); 2) parallel. In the first case the defects attract each other and then disappear, in the second case they repel each other. So we have to conclude that the cylindrical defect  $P_{+2}^c$  is not stable: it decays into the R- and H-defects with parallel axes of symmetry, then such a reorientation of the defects takes place so that the force of interaction changes its sign, and after that they annigilate creating undistorted structure with zero elastic energy.

\*Supported by RBRF Grant 95-02-05974a

**D4P.64** 

THE R- AND H-DEFECTS IN A CYLINDRICAL CAPILLARY, <u>V.K.Pershin</u> and T.V.Kushnareva<sup>\*</sup>, Department of Physics, Cheliabinsk State University, 454136 Br.Kashirin str., 129, Cheliabinsk, Russia

Having based on analysis of solution of equilibrium equation for nematic liquid crystals, we have considered the physical pattern of structural instability of linear disclination (S = +1). It has been shown that in a capillary there occurs either the radial point defect or the hyperbolic one, or a system of alternating sequences of them, rather than non-singular "escaping" disclination as it was claimed before [1]. We have studied the special features of elastic field of such bound defects in comparison with the field of the same free defects. Their energies have been computed and it has been stated that the influence of the boundary causes the energy gap between the radial and hyperbolic defects to be reduced approximately by half.

[1] P.E. Cladis, M. Kleman, J.de Phys., 33, 591 (1972).\*Supported by RBRF Grant 95-02-05974a

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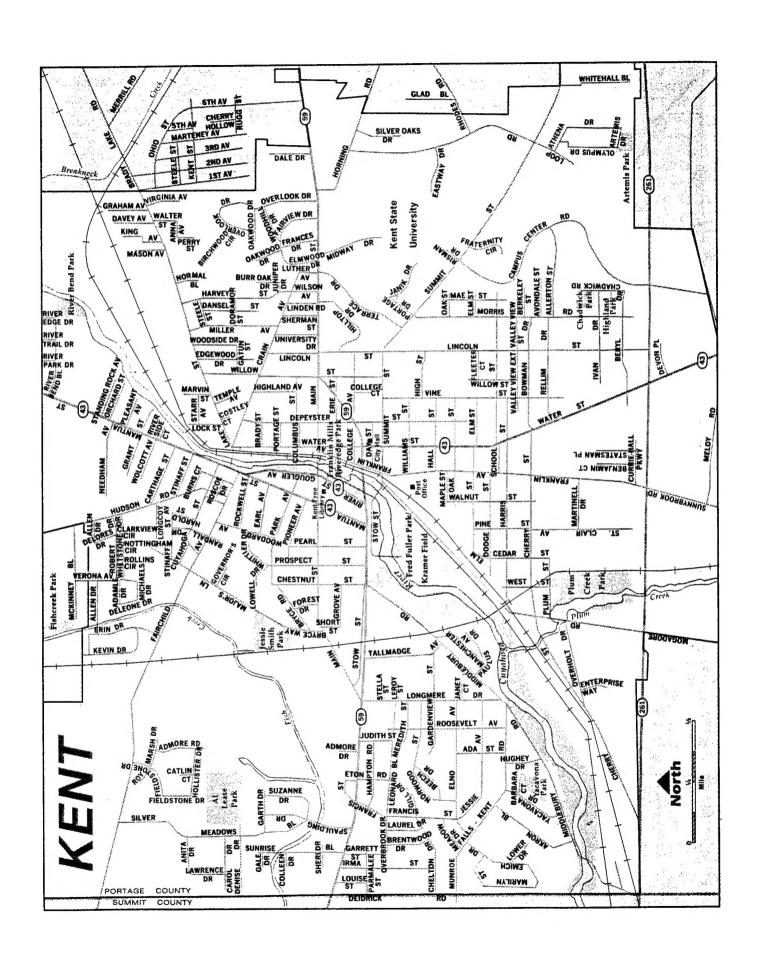
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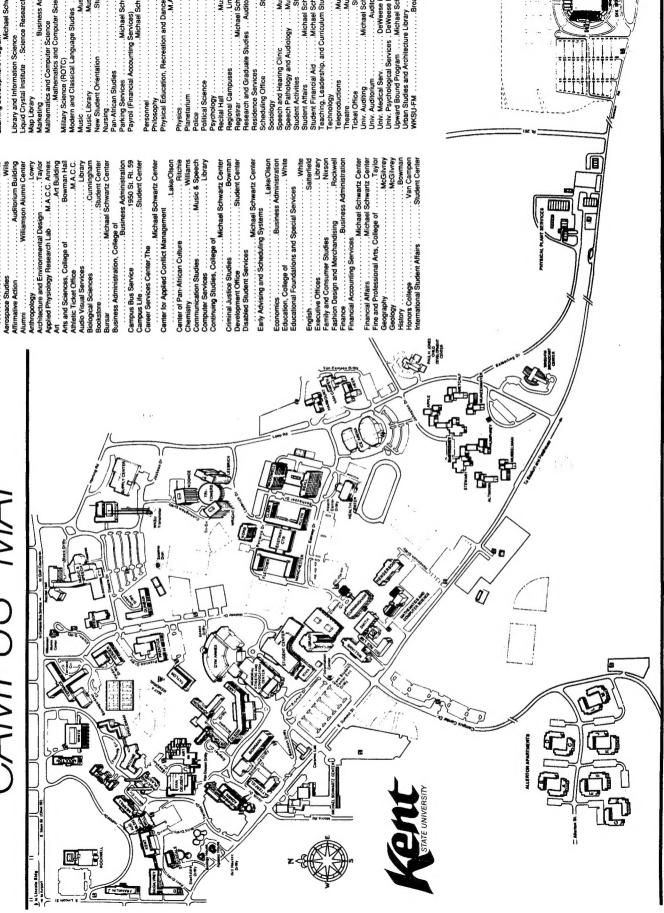
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